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THE ABSORPTION SPECTRA OF SOLUTIONS OF A NUMBER OF SALTS IN WATER, IN CERTAIN NON-AQUEOUS SOLVENTS, AND IN MIXTURES OF THESE SOLVENTS WITH WATER.

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[TWENTY-FOURTH COMMUNICATION.]

(The following paper records some of the results obtained in an investigation on the absorption spectra of solutions carried out under a grant from the Carnegie Institution of Washington. The work as a whole is now being published by the Institution,[1] and much of this paper is taken directly from that publication.)

INTRODUCTORY.

The work on the absorption spectra of solutions, of which this forms a part, was begun in the fall of 1905 and continued during the year 1905–6 by Jones and Uhler. The results obtained are given and discussed in Publication No. 60 of the Carnegie Institution of Washington, entitled "Hydrates in Aqueous Solution," by H. C. Jones.[2] The first part of that

[1] Carnegie Institution Publication, No. 110 (1909).

[2] Cf. THIS JOURNAL, **37**, 126, 207 (1907).

work dealt with the effect of adding various dehydrating agents to solutions of colored salts; the second part, with the change in the absorption spectra produced by adding water to nonaqueous solutions. In the latter phase of the work, however, the concentration of the colored salt was varied in the solutions used in making any one spectrogram; but as the change in the spectrum observed was always the same qualitatively as would be expected from the change in concentration, it was deemed advisable to carry out again this part of the earlier work, keeping the concentration of the colored salt constant.

The salts used in the previous investigation were: Cobalt chloride, copper chloride, and copper bromide. In this investigation cobalt bromide was added to the above list of compounds. The spectrograms we have obtained show the same general change in the absorption as was observed in the earlier work, thus proving that it was not due to change in concentration, but to some action of the water added.

If we assume that the absorption of light is due to vibrating, charged particles, or electrons, which are associated with ions, molecules, or groups of one or both of these, it is natural to expect that the character of the absorption will, in general, depend upon the nature of the system with which the vibrating, charged particle is associated. In what follows, the system made up of the charged particle and whatever it is associated with will be spoken of simply as the "absorber."

The simplest case of an absorbing solution would be one containing only one kind of "absorber," and we shall speak of it as a "simple" absorbing solution. Such a solution does not in all probability exist, but is perhaps closely approached in such cases as the very dilute solutions of the salts of permanganic acid studied by Ostwald and others. Such a solution the absorption of light of a given wave length would be simply proportional to the number of absorbers in the path of the light (Beer's law); and if the absorbers are not changed by adding more of the solvent it follows at once that if the product of concentration and thickness of layer of the solution is kept constant, the absorption will be unchanged. Also, if we have a solution containing several kinds of absorbers,

each acting independently of the others, the same statement would be true; in other words, the absorption spectrum of a mixture of simple solutions will be the sum of the absorption spectra of the constituents.

If the concentration is very great, the absorbers may be so close together that they cease to act independently of each other; in such a case, even if the solution is a simple absorbing one, Beer's law *may* cease to hold. In general, however, we may say that for simple absorbing solutions or mixtures of these, Beer's law will hold.

Actual solutions always differ more or less from the ideal simple solutions on account of the changes produced by dilution. These changes are due to *association*, *dissociation*, and *solvation*.

The molecules of the dissolved substance may combine with each other, forming more or less complex aggregates, each of which will, in general, have its own peculiar power of absorbing light. The composition of the aggregates will depend upon temperature and concentration, and hence, if a solution containing such aggregates is diluted, we should expect to find deviations from Beer's law even if the temperature is kept constant.

The molecules of a great number of substances, when dissolved, dissociate into two or more ions, the amount of dissociation depending upon the concentration. It is to be expected that the absorption of the ions into which a molecule dissociates will be different from that of the molecule itself; and, consequently, on diluting an electrolyte we should expect to find deviations from Beer's law, unless the solution is so dilute that it may be considered as completely dissociated.

We may also have various combinations of molecules, aggregates of molecules or ions, not only with each other, but also with the molecules of the solvent, the nature of which will depend both on temperature and concentration, and each of which may have a different power of absorbing light. If a simple, colored electrolyte like cobalt chloride, for example, is dissolved in water, we see at once what a complicated system the solution is; and it is not surprising that, in spite of the

great amount of work which has already been done on this one salt alone, we are still far from being able to give a satisfactory account of its absorption spectrum.

A satisfactory account of the absorption of any salt in solution requires a knowledge of the kinds of absorbers the salt forms, and of the amount of each for any given set of conditions. Given this knowledge, it would be necessary to determine what would be the absorption spectrum if the solution contained only one kind of absorber. This could be done as follows: Suppose a salt in solution gives rise to the absorbers A, B, C, D, E, etc., the amount of each of which is supposed to be known under all conditions of temperature, pressure, concentration, etc. Vary the conditions in such a way that all the absorbers except A, for example, are kept constant, and note the change in the spectrum; this change is due to A alone, since by hypothesis no other absorber is varied. Repeat, keeping all except B constant, and so on. By this process of elimination we should eventually arrive at a complete knowledge of the absorption due to each absorber, and could hence predict exactly what would be the absorption of any solution whatever of the salt in question. Unfortunately our knowledge of the parts formed when a salt is dissolved is still very vague.

We have methods for measuring dissociation, so we may regard the number of ions and the number of undissociated molecules as known for different conditions. Regarding aggregates and solvates, however, our knowledge is very general, indeed. Determinations of molecular weight give some idea concerning the existence or nonexistence of aggregates, and the methods of Jones and others furnish similar ideas about solvates; but the knowledge gained thus far is not definite enough to enable us to perform experiments along the lines indicated above. A great deal can, however, be learned not only about absorption, but also about the nature of solutions, by the study of absorption spectra under conditions which are varied as much as possible.

The methods commonly employed are:

(1) To keep the concentration constant, varying the depth of the cell and photographing the spectra of successive depths

one beneath the other, so that the complete spectrogram gives an idea of the intensity of absorption for the different regions of the spectrum, besides locating the absorption bands.

(2) To keep the depth of cell constant and vary the concentration. The results here should be identical with those obtained by keeping concentration constant and varying the depth of cell, provided the solution is of such a nature that Beer's law holds; in general, however, the two methods give quite different results, owing to the change in the nature of the absorbers produced by dilution.

Another method is that followed in the present work, namely, to vary both depth of layer and concentration in such a manner that the product of the two remains constant. If the nature of the absorbers is not changed by dilution, this method leaves the number of absorbers in the path of the beam of light constant, and hence the spectrum for successive solutions should be identical; or, what amounts to the same thing, the width of the absorption bands, as shown by the spectrogram, should remain constant throughout. Any deviation from Beer's law would at once be seen in a change in width or position of the bands as the concentration is varied.

A variation of this method also employed in the present work is to vary the depth and concentration in such a manner that the total number of ions or the total number of undissociated molecules in the path of the beam of light remains constant. This is easily done as follows: Let the concentration be denoted by c, the ratio of the number of dissociated molecules to the total number in solution by x, the depth of solution used by d; the number of ions in a cubic centimeter of the solution is then proportional to cx, and the number of undissociated molecules to $c(1-x)$. To keep the number of ions in the path of the beam of light constant it is only necessary to keep the product cxd constant; and to keep the number of undissociated molecules constant the product $c(1-x)d$ must remain constant. If the successive depths of solution to be used have been fixed arbitrarily, the required concentrations are determined in the following way: From tables giving the values of x for different values of c the products cx and

$c(1 - x)$ are calculated for all values of c. Two curves are then plotted, one between cx and c, the other between $c(1 - x)$ and c. Letting c_1, x_1, and d_1 represent the values of c, x, and d for the greatest concentration to be used, the values for any other concentration being represented by the same letters without subscripts, we have

$$c_1x_1d_1 = cxd, \qquad c_1(1 - x_1)d_1 = c(1 - x)d,$$

or,
$$cx = \frac{c_1x_1d_1}{d}, \qquad c(1 - x) = \frac{c_1(1 - x_1)d}{d},$$

respectively.

The terms on the right are both known and hence the products cx and $c(1 - x)$ for any chosen value of d can be determined, and from the two curves the corresponding values of c may be read off directly.

Since more is known about dissociation than about association or solvation, it is only natural to try to see whether the observed changes in absorption can be explained by dissociation alone. If dissociation does not suffice, then we must conclude that other factors come in. The present work is devoted largely to a study of the absorption spectra of a large number of salts from the standpoint of dissociation.

Let us consider for a moment the kind of evidence obtained by the methods outlined, and what conclusions may be drawn from them. Consider first the possibility that an absorption band does not change in width or position with concentration, when the product of depth of layer and concentration is kept constant. The simplest explanation is that the absorption of the molecule and of the ions into which it breaks down on dissociation is the same. An excellent example of this type is furnished by the ultraviolet band of nickel sulphate; also by the more dilute solutions of neodymium and praseodymium chloride.

Let us now consider cases where we have deviations from Beer's law. Take first the possibility that an absorption band widens with dilution, when the product of concentration and depth of layer is kept constant. This would indicate either that the band is due to ions, or that the ions have stronger

absorption in the region considered than the undissociated molecules. By making a series of photographic exposures, keeping the number of ions in the path of the beam of light constant, we can decide between the two possible explanations. If the band now remains constant in width and position, it is most likely due to ions alone; if it narrows on dilution, it is due both to ions and molecules, but the ions have stronger absorbing power than the undissociated molecules; while if the band should widen with decrease in concentration, dissociation would in no way suffice to explain it.

The other case is where the band narrows with dilution, when the product of concentration and depth of layer is kept constant. If dissociation can account for this we must either have the undissociated molecules absorbing more strongly than the ions formed from them, or else the ions not absorbing at all. In the former case the band should widen with dilution when "undissociated molecules" in the path of the light are kept constant, while in the latter case the band would remain constant in width and position under the same conditions. If the band narrows with decrease in concentration when the number of undissociated molecules is kept constant, dissociation alone can not possibly explain the facts. An example of this case is furnished by the ultraviolet absorption of most copper salts in aqueous solution.

A case often met with in the present work is where a band narrows with dilution when the product of concentration and depth of layer is kept constant, but widens when the number of undissociated molecules is kept constant. This deserves further consideration, as dissociation may or may not be able to account for it, depending on the nature of the change in the band. The case was discussed by E. Müller, who showed that by measurements with a spectrophotometer of the extinction coefficient at various concentrations, we may determine whether Beer's law holds for each one of the three absorbers in a solution of an electrolyte, even when these have quite different powers of absorption. Work on this point is now in progress with the solutions showing the effect just spoken of, and the results will be published shortly.

Another interesting method of studying absorption spectra is to keep both concentration and depth of layer constant, and to vary the temperature. Much work of this kind has already been done by Hartley and others, and a similar investigation is now in progress in this laboratory. As is well known, change of temperature has only a small effect on the dissociation, hence we may say that when the temperature is varied the dissociation remains nearly constant. The spectrum of some solutions, however, undergoes very great changes; for example, solutions of cobalt chloride which are red at room temperatures become blue when the temperature is elevated sufficiently; and according to Donnan and Bassett solutions of the same salt in ethyl alcohol, which at ordinary temperatures are blue, turn red when cooled down to —75° C. This effect, which involves the appearance or disappearance of a complicated set of absorption bands in the red, can evidently not be accounted for by dissociation, since it is observed when the dissociation is known to change but very slightly.

In the present work considerable attention has been given to solutions in nonaqueous solvents, such as methyl alcohol, ethyl alcohol, and acetone, as well as to solutions in mixtures of these solvents with water. In this part of the work great care has been taken to have both the salts and solvents as free from water as possible, and this is of fundamental importance, as is shown by the spectrograms of solutions of neodymium chloride in mixtures of alcohol and water, where it appears that the change in the spectrum produced by 1 per cent or less of water may easily be detected.

The question of the effect of the solvent comes up in this connection, and this in turn involves the more general question as to the condition of a molecule of a dissolved substance in any solvent whatsoever. Does it form some kind of a compound with the solvent, or does it move about freely in the solvent without materially changing its nature? Kundt's law, which states that the effect of the solvent upon absorption is simply to shift the position of the absorption bands, these being located nearer the region of long wave lengths the greater the dispersion of the solvent, seems to imply that the molecule

of the dissolved substance exists in the free state in solutions. If this view be taken, then the effect of the solvent should not be very great, especially if solutions in solvents having similar optical properties are compared. If, on the other hand, a salt, when it goes into solution, always forms some sort of a compound with the solvent, we might expect to find that solution produces radical differences in the absorption.

It is evident that a study of the absorption spectra of a salt, when dissolved in various solvents, ought to bring out many points of interest bearing upon the question of the nature of solutions.

Apparatus.

For visual examination of solutions a small, direct-vision, grating, pocket spectroscope was always at hand, and was found very useful for the purpose of determining what particular range of concentrations it was desirable to work with. Judging from the color of the solution as seen by the unaided eye was found to be very unsatisfactory, since many solutions have very wide absorption bands which may give the solution quite a decided tint, even when the absorption is so feeble that it would be almost impossible to obtain a satisfactory photographic record of it. On the other hand, when solutions have narrow, intense absorption bands, like those of the salts of the rare earth metals, the solution may show practically no color to the unaided eye and still the absorption bands may be quite intense as seen in the spectroscope.

For photographing the spectra, the vertical grating spectrograph used by Jones and Uhler was employed. In its original form as used by them, films 2.5 by 7 inches, on which the spectrum from λ 2000 to λ 6300 could be registered, were employed.

In the present work it was decided to remodel it so as to allow the whole spectrum from λ 2000 to λ 7600 to be photographed, and accordingly the camera and the camera end of the box were enlarged so as to hold films 2.5 by 9 inches. Owing to the fact that the grating has only 10,000 lines to the inch, it was not possible to add the extra 2 inches to the

red end of the camera. If this could have been done, it would have left the grating axis very near the middle of the spectrum. The 2 inches were actually added to the ultraviolet end, which necessitated turning the grating axis farther away from the slit, thus placing it in a point of the spectrum some little distance beyond the visible violet. The spectrum is, however, near enough to normal, even at the extreme red end, to make any correction unnecessary, unless measurements of a very high degree of accuracy are required.

For holding the aqueous solutions, the cell illustrated in Fig. LXVI.,[1] page 172, of "Hydrates in Aqueous Solution," was employed throughout, while for nonaqueous solvents the cell shown in Plate XXII.[2] of the same work was used.

Photographic Material, Etc.

It was at first decided to use films coated with the panchromatic emulsion made by Wratten and Wainwright, of Croyden, England, as this emulsion has been found to be very uniformly sensitive to light of all wave lengths between λ 2000 and about λ 7400. The makers, however, did not succeed in producing a satisfactory film in time for the present work, and hence it was necessary to use the Seed L-orthofilm for the region from λ 2000 to about λ 6000, and to make a separate exposure for the red end of the spectrum, using for this purpose Wratten and Wainwright panchromatic glass plates, cut to such lengths (4 to 4.5 inches) that the curvature of the focal plane would not introduce any appreciable difficulty. This method very nearly doubled the time and work necessary to make the spectrograms, as two separate sets of exposures had to be made with each set of solutions. It also made it very difficult to get the two negatives of such intensities that they would match satisfactorily, owing not only to the different absolute sensibility of the two emulsions to light of a given wave length, but also to the different rates at which the photographic blackening increases with time for the two emulsions.

[1] Cf. THIS JOURNAL, **37**, 141 (1907).
[2] Cf. *Ibid.*, **37**, 247 (1907).

The developer used throughout was a concentrated hydroquinone solution made up according to Jewell's formula.[1]

Sources of Light.

The most satisfactory source of light for the region of the spectrum lying between the extreme red and the beginning of the ultraviolet is the Nernst lamp, as it is brilliant enough to bring the necessary time exposure down to about a minute, and is, of course, perfectly continuous and steady. In the ultraviolet it has been shown that its action decreases rapidly with the wave length, ceasing practically at about λ 3200. For this region, then, some spark spectrum must be used. The cadmium-zinc spark used by Jones and Uhler is fairly satisfactory, being especially strong in the extreme ultraviolet, but it has the disadvantage of having a limited number of very intense lines on a rather faint, continuous background. It was hoped that some spark spectrum could be found having a very large number of lines, but without any lines of very great intensity.

A reference to published tables of the spectra of the elements showed that tungsten, molybdenum, and uranium all satisfy this requirement. Each of these has so many lines, and these so closely packed, that with an instrument of moderate dispersion the spectrum ought to be nearly continuous. The problem was to make spark terminals of these substances which could be used satisfactorily. The metals not being easily obtainable, the following plan was tried: Sheet carbon about 3 mm. thick was cut into pieces about 1 cm. by 4 cm. and dipped in concentrated solutions of ammonium molybdate, or uranium nitrate; a suitable solution of a tungstate was not tried. These pieces of carbon were then heated to redness in a Bunsen flame and again quickly immersed in the solution, the process being repeated two or three times. Some pieces were also treated with solutions of salts of iron, copper, and cobalt, and others were treated with two or more of the solutions in succession. The spectra of these carbon terminals showed the lines of the metals with which they were

[1] Astrophys. J., **1900**, 240–243.

treated almost as well as terminals of the metals themselves; but in the case of iron, copper, or cobalt the cyanogen bands were also observed. With molybdenum and uranium, however, the cyanogen bands did not appear, the merest trace of the λ 3883 band being detected. The uranium spectrum is almost continuous with the dispersion employed, but its intensity falls off very rapidly from λ 3000 toward the ultraviolet. The molybdenum spectrum, although not so nearly continuous, is much richer in ultraviolet, being quite strong as far as λ 2300

Curiously enough, if a pair of carbon terminals is treated with molybdenum and also with one or more of the other metals, very little except the molybdenum spectrum is seen. Uranium, however, seems to increase the intensity of the continuous background somewhat, and hence the terminals finally used were prepared by dipping them twice in the molybdate solution and then three times in the solution of uranium nitrate.

It was also found that the terminals charged with various metals wore away at quite different rates when the spark was passed. Those dipped in a solution of copper wore away at the rate of a millimeter or more per minute, while those treated with molybdenum could be used for hours without appreciable wear. The character of the spectrum given by these molybdenum-uranium terminals may be seen from any of the plates reproduced in the following sections which do not show complete absorption in the ultraviolet.

The coil used to produce the spark was a large Röntgen X-ray coil, through the primary of which was passed an alternating current of from 5 to 8 amperes, 60 cycles; and across the secondary terminals was shunted a capacity of about 0.011 microfarad. The spark used was about a centimeter in length, and was placed about 15 cm. above the slit, the direction in which the spark passed being perpendicular to the length of the slit. By this arrangement the grating received light from all parts of the spark at the same time. In order to produce a uniform photographic strip of the proper width, it was necessary to keep the spark terminals moving in a direc-

tion parallel to the length of the slit, which was done by hand, a suitable stand being used. Care was taken to move the sparkholder always at the same rate, namely, a to-and-fro motion in about 4 seconds, which insured equality in times of exposure for the different strips of the spectrograms. The intensity of the spark undoubtedly varied somewhat, due to fluctuations of the voltage impressed upon the primary terminals of the coil; but this was found to be so small that no provision was made for regulating it. The Nernst filament is, however, so sensitive to slight changes in voltage that a variable resistance was placed in series with it; by regulating this the current was always kept at 0.8 ampere during an exposure.

Making a Spectrogram.

In making a spectrogram consisting of seven photographic strips with a comparison spectrum, the following was the usual sequence of operations: Seven separate solutions were made up, the quantity of each being usually 25 cc. The cell to be used having been cleaned and dried, was filled to the required depth with the most concentrated solution of the series, and the quartz plates limiting the depth of the solution adjusted to parallelism. The exposure to the Nernst lamp was then made, the current being kept at 0.8 ampere by hand regulation of the variable resistance in series with it. The usual time of this exposure was 1 minute. An opaque screen covering up the visible spectrum as far down as λ 4000 was then interposed between the grating and the photographic film, and the exposure to the light of the spark in the ultraviolet was made. The duration of this exposure was usually 2 minutes. The photographic film was then moved a distance of 6.5 mm. into the proper position for the next exposure. The cell was emptied and rinsed out with a few drops of the next solution, and the series of operations repeated for the second strip, and so on. It was always found advisable to clean the slit jaws after exposure, and also to see that the image of the Nernst filament fell in the proper position on the slit.

After the film had been exposed and the comparison spark spectrum impressed, it was necessary to make a series of exposures on a panchromatic plate for the red end of the spectrum, using the same set of solutions. No exposure to the spark was made in this set except for the narrow comparison strip. As the extreme end of the plate was at about λ 7600, λ 3800 of the second order would overlap the first order here. Accordingly an absorbing screen was always used in making the exposures for the red end of the spectrum. This screen consisted of two glass plates separated by a layer of Canada balsam a little less than a millimeter thick. It absorbed all radiations of shorter wave length than λ 3900.

The scale accompanying the spectrograms in the following chapters was made by photographing an ordinary paper scale. Several photographs were made, the distance between the paper scale and the lens of the camera being varied slightly from exposure to exposure. The negative which fitted the majority of spectograms best was selected and used throughout. Absolute accuracy is not to be expected, owing to the fact that both photographic films and the paper on which prints from these were made contract more or less in drying, and different films or papers contract differently. λ 5000 on the scale was always placed in coincidence with the corresponding wave length on the photographic strips; the correction for the ends of the spectrograms differs slightly for the different plates, but never amounts to more than about 25 or 30 Ångström units.

SALTS OF COBALT.

Jones and Uhler,[1] in their work on the absorption spectra of salts of cobalt and copper, discussed a number of the more important papers dealing with cobalt, so that it is necessary only to make brief reference to them here.

Babo[2] observed a number of the color changes produced in cobalt salts by change in temperature, or by addition of a de-

[1] Publication No. 60, Carnegie Institution of Washington.
[2] Jahresb., 1857, 72.

hydrating agent. Similar observations were made by Gladstone[1] and Schiff.[2]

Bersch[3] proposed the view that there are two modifications of the compound $CoCl_2.6H_2O$—the one red and the other blue—which would thus account for the color changes in cobalt salts with rise in temperature.

Tichborne[4] would also account for these color changes on the basis of hydration, and Vogel's[5] work pointed in the same direction.

The investigations of Russell[6] on the absorption spectra of solutions of cobalt salts is important. He worked under various conditions, such as with the fused salt, with its solution in concentrated hydrochloric acid, and with solutions in the various alcohols and glycerol. He also studied the effect of changes in temperature on the absorption spectra. He concluded, as the result of all of his work, that the color of the aqueous solutions was due to the presence of hydrates.

Potilitzin[7] showed that the conclusion of Bersch, that there are two modifications of the compound $CoCl_2.6H_2O$, is an error, and that the formation of blue cobalt chloride from the red modification is always a dehydration phenomenon.

Etard[8] studied the color changes and also the solubility curve of cobalt chloride and iodide, and showed that the sudden changes in the direction of the solubility curves indicated the existence of various hydrates of these salts. He also studied the changes in the absorption spectra of cobalt chloride with changes in temperature.

Engel[9] does not believe that any general theory can be advanced to account for the changes in color of cobalt salts, but thinks that the blue color is often due to the formation of double compounds. The blue color of a hot, saturated solution of cobalt chloride, he believes, is due to a double com-

[1] J. Chem. Soc., **10,** 79 (1859).
[2] Ann. Chem. (Liebig), **110,** 203 (1859).
[3] Sitzun. Wien [2], **56,** 726 (1867).
[4] Chem. News, **25,** 133 (1872).
[5] Ber. d. chem. Ges., **8,** 1533 (1875); **11,** 913 (1878); **12,** 2313 (1879).
[6] P. Roy. Soc., **32,** 258 (1881); Chem. News, **59,** 93 (1889).
[7] Ber. d. chem. Ges., **17,** 276 (1884); Bull. Soc. Chim. [3], **6,** 264 (1891).
[8] Compt. rend., **131,** 699 (1891); **120,** 1057 (1895).
[9] Bull. Soc. Chim. [3], **6,** 239 (1891).

pound between the salt and the hydrochloric acid liberated as the result of hydrolysis.

Wyrouboff[1] and Le Chatelier[2] show that Engel's view is untenable.

W. N. Hartley,[3] in his elaborate investigations of absorption spectra, has included a number of salts of cobalt. His experimental work consisted in observing and photographing the spectra of a large number of solutions of chlorides, bromides, iodides, nitrates, etc., of a fairly large number of metals, including cobalt. Some of the more interesting and important conclusions at which he arrived, stated nearly in his own words, are the following:

When a definite crystalline hydrate is dissolved in a non-aqueous solvent, upon which it does not act chemically, the molecules of the salt remain unchanged in chemical composition.

In a series of anhydrous salts which do not form definite crystalline hydrates, the effect of rise in temperature up to 100° C. does not produce any alteration in their absorption spectra other than that which results with substances which undergo no chemical change with such rise in temperature. The change in question is usually an increase in the intensity of the absorption, or a slight widening of the absorption bands.

Crystallized hydrated salts dissolved in a minimum amount of water at 20° C. undergo dissociation when the temperature is raised. The extent of the dissociation may proceed as far as complete dehydration of the compounds, so that more or less of the anhydrous salt may be formed in the solution.

The most stable compound that can exist in a saturated solution at 16° C. or 20° C. has not always the same composition as the molecule of the crystallized solid at the same temperature, since the solid may undergo a partial dissociation from its water of crystallization when the molecule enters into solution. When a saturated solution of a colored salt suffers a great change in color or any remarkable change in

[1] Bull. Soc. Chim. [3], **6**, 3 (1891).

[2] *Ibid.* [3], **6**, 84 (1891).

[3] Trans. Roy. Dub. Soc. [2], **7**, 253–312 (1900); J. Chem. Soc., **81**, 571 (1902); **83**, 221 (1903).

its absorption spectrum upon dilution, the dilution is always accompanied by marked evolution of heat.

Hartley[1] closes his paper on "The Absorption Spectra of Metallic Nitrates" with the following significant paragraph:

"The ultimate conclusion drawn from this work is that the operations of dissolving a salt and diluting the solution do not cause a separation of the compound into ions, but only a dissociation of such a character that the molecule is shown to consist of two parts, the movements of the one being influenced by those of the other, so that the molecule of the salt is, in fact, not completely resolved into ions, but is in a condition of molecular tension. The application of external energy, such as light or electricity, may, however, readily cause a separation such as may be brought about by electrolysis or by static electricity, and, in some instances, by photographic action."

Ostwald[2] thinks that the red color of solutions of salts of cobalt is due to the cobalt ions.

The paper of Donnan and Bassett[3] should be especially mentioned in connection with the changes in color of cobalt salts. After citing a number of well-known facts, and adding a fairly large number of interesting new ones, they came to the conclusion that the blue color of solutions of cobalt salts is due to the formation of complex anions containing cobalt. Some of the evidence which they furnish merits very careful consideration in this connection.

Hartley[4] takes issue with the conclusions reached by Donnan and Bassett, interpreting the facts cited or discovered by them in terms of hydration and dehydration.

A fairly large number of salts of cobalt has been brought within the scope of this investigation. Thus, plates have been obtained for cobalt chloride in water—to test Beer's law; cobalt chloride in water—number of ions in the path of the beam of light constant; cobalt chloride in water—molecules constant; cobalt chloride in methyl alcohol—Beer's law;

[1] J. Chem. Soc., **83,** 245 (1903).
[2] Grundlinien d. anorg. Chem., p. 620.
[3] J. Chem. Soc., **81,** 939 (1902).
[4] *Ibid.*, **83,** 401 (1903).

cobalt chloride in ethyl alcohol—Beer's law; cobalt chloride in acetone—Beer's law; cobalt chloride in methyl alcohol to which water is added; cobalt chloride in ethyl alcohol to which water is added; cobalt chloride in acetone to which water is added; cobalt bromide in water—Beer's law; cobalt bromide in water—molecules constant; cobalt bromide with calcium bromide; cobalt bromide in methyl alcohol—Beer's law; cobalt bromide in ethyl alcohol—Beer's law; cobalt bromide in acetone—Beer's law; cobalt bromide in methyl alcohol to which water is added; cobalt bromide in ethyl alcohol to which water is added; cobalt bromide in acetone to which water is added; cobalt nitrate in water—Beer's law; cobalt nitrate in water—molecules constant; cobalt sulphate in water—Beer's law; cobalt sulphocyanate in water—Beer's law; cobalt sulphocyanate in water—molecules constant; cobalt acetate in water—Beer's law.

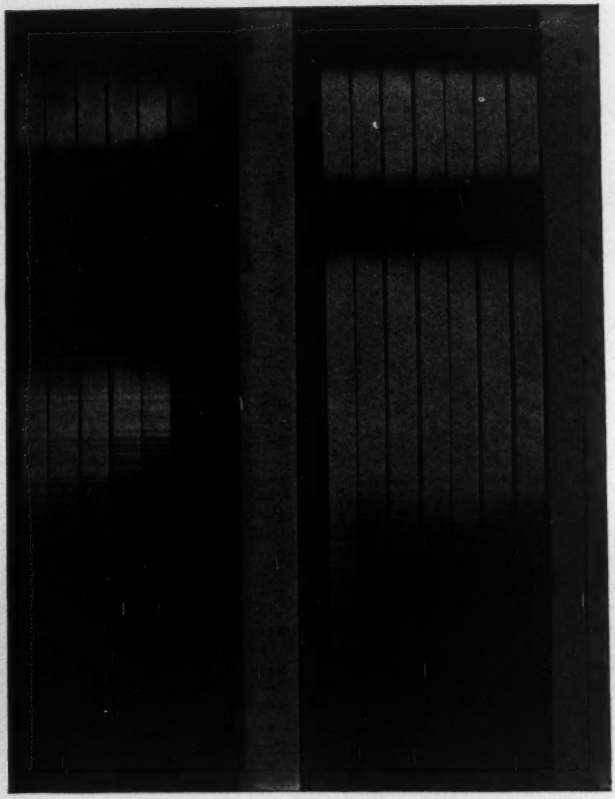
In all twenty-three complete plates, all of which are given in the Carnegie Publication,[1] were made with salts of cobalt. Only three are reproduced in this paper.

Cobalt Chloride in Water—Beer's Law (*See Plate I., A and B*).

In both A and B, the strip corresponding to the most concentrated solution is adjacent to the numbered scale. The concentrations of the solutions used in making set A were 2.5, 1.88, 1.25, 0.83, 0.58, 0.42, and 0.31, respectively; the corresponding depths of cell were 3, 4, 6, 9, 13, 18, and 24 mm. The concentrations used in making set B were 0.83, 0.63, 0.42, 0.276, 0.192, 0.139, and 0.104; the depths of cell were the same as in set A. The exposures to the red end of the spectrum were omitted in this case, inasmuch as observations with the direct-vision spectroscope showed that the solutions, at least in such thicknesses of layer as were employed, were perfectly transparent from the beginning of the orange to the end of the red. The most concentrated solution in layers of 2 cm. or more showed faint traces of bands in the orange and red, but in layers of a few millimeters thickness these were, of course, quite invisible.

[1] Carnegie Institution Publication, No. 110.

Plate I.



A B

The spectrogram shows three regions of absorption; one in the green, middle near λ 5200; one in the ultraviolet, with its middle near λ 3300; and one in the extreme ultraviolet. The strips corresponding to the four most concentrated solutions of set A show only one absorption band in the ultraviolet, but the strip corresponding to the fifth solution shows transmission between λ 2800 and λ 3000, and absorption from λ 3000 to λ 3500, thus making it very evident that there are two regions of absorption. The strips corresponding to the three most concentrated solutions of set B also show very plainly the existence of the band at λ 3300, although the absorption is not complete even at the middle of the band. In the fourth strip of B, corresponding to a concentration of 0.276 and depth of cell equal to 9 mm., practically all trace of the band has disappeared, the spark spectrum appearing to shade off uniformly from λ 3600 to λ 2650, where it ends.

It will be noticed that the intensity of the spark spectrum in the region λ 2900 is greater for the strips near the numbered scale than for the fourth, fifth, and sixth strips. This is due partly to a gradual decrease in the intensity of the spark itself while the spectrogram was being made, produced by a gradual fall in potential of the source of alternating current operating the coil. That the effect is real, however, is shown by another plate, where a similar decrease in transmission at λ 2900 with dilution is recorded, and where the intensity of the spark was constant or very nearly so throughout. The increased intensity of the seventh strip of Plate I., B is due to the fact that before making the exposure the potential was readjusted to its original value.

The absorption in the extreme ultraviolet decreases regularly with dilution, the strip corresponding to the most concentrated solution in set B transmitting as far as λ 2650, while that corresponding to the most dilute solution shows transmission a little below λ 2500.

In set A the band in the green narrows quite rapidly at first, then more slowly with dilution. In set B it remains very nearly constant, especially in the strips corresponding to the more dilute solutions.

The facts brought out by the spectrogram may be summed up briefly as follows: When the product of concentration and depth of absorbing layer is kept constant, the absorption band in the green remains constant, except in very concentrated solutions, where it narrows somewhat with dilution; the one-sided, extreme ultraviolet absorption decreases with dilution, while the band having its center near λ 3300 narrows very rapidly with dilution, disappearing entirely when a concentration of about quarter normal is used in a layer about 1 cm. in depth. In the region λ 2800 to λ 3000 there is remarkable transparency in solutions having a concentration about half normal. This transparency decreases somewhat with dilution to about one-tenth normal.

A comparison between this plate and Plate II. in the work of Jones and Uhler, already referred to, reveals a remarkable difference in the ultraviolet. The four strips nearest the comparison spectrum of their plate correspond to concentrations of more than 2.0 normal, with a depth of absorbing layer of 0.67 cm., and yet the absorption in the region λ 3000–λ 3500 is not very great. It might at first sight seem probable that the absorption band in this region was produced by some impurity in the cobalt chloride used. But this is improbable, since the salt from which were obtained the solutions used by Jones and Uhler and those used in the present work came from the same sample of material. Besides, Plate XXIII., in "Hydrates in Aqueous Solution," shows that the solution of the cobalt chloride used by Jones and Uhler, when dissolved in methyl alcohol, exerts strong absorption in the ultraviolet, while Plate I. of the present work indicates only faint absorption in this region, although the concentrations, depth of cell, etc., used in the two cases, did not differ materially; hence, it is evident that it is not a question of the presence of an impurity. The probable explanation is that the discrepancy is due to a difference of temperature.

It is well known that the absorption of cobalt salts in solution is greatly affected by even slight changes in temperature, and if the λ 3300 band is especially sensitive, such variations of temperature as occur in the laboratory on different

Plate II.

A B

days might be sufficient to account for the change in the spectrum observed. No data are at hand, however, giving the change of absorption in the ultraviolet produced by change of temperature, and hence this point will have to remain unsettled until the work now in progress shall have supplied the data for the absorption band in question.

Cobalt Chloride in Ethyl Alcohol—Beer's Law (See Plate II.).

The concentrations of the solutions used in making the negative for A were 0.15, 0.126, 0.104, 0.086, 0.071, 0.060, and 0.050; the corresponding depths of cell were 8, 9.5, 11.5, 14, 17, 20, and 24 mm., respectively. For B the concentrations were 0.060, 0.050, 0.042, 0.034, 0.028, 0.024, and 0.020, the corresponding depths of cell being the same as those used in making set A.

The color of the solutions, as seen in the bottles, was deep blue for the most concentrated, changing to a light greenish-blue for the most dilute. The general absorption observed in the concentrated solutions in methyl alcohol was quite absent in the ethyl alcohol solutions, so that in making the negatives for both A and B the slit was adjusted to a width of 0.01 cm. and the exposures to the Nernst lamp and spark were 1.5 and 3 minutes, respectively.

The spectrogram shows a region of absorption in the extreme ultraviolet which narrows regularly with dilution; the limits of transmission for the strips corresponding to the most concentrated and most dilute solutions of set A are λ 2670 and λ 2630, respectively, while for set B they are λ 2580 and λ 2550.

The negative for set A also shows two absorption bands in the ultraviolet, having their centers approximately at λ 3100 and λ 3600. These bands are undoubtedly identical with those already noted in the same region for the solution in methyl alcohol. One difference, however, is to be noted. The bands in the ethyl alcohol solutions are somewhat more intense, in spite of the fact that the concentration of the colored salt is smaller, and they also disappear much more slowly with dilution.

The absorption in the green is very much fainter in ethyl alcohol than in methyl alcohol, and measurement of the position of the center of the band indicates that it is located a trifle nearer the red in the former case. The position of the center was found to be at λ 5280. The band remains constant in width and position with dilution; A shows a region of intense absorption in the yellow, orange, and red, which narrows somewhat with decrease in concentration; the limits of transmission for the most concentrated solution are λ 5500 and λ 7170, and for the most dilute, λ 5500 and λ 7060.

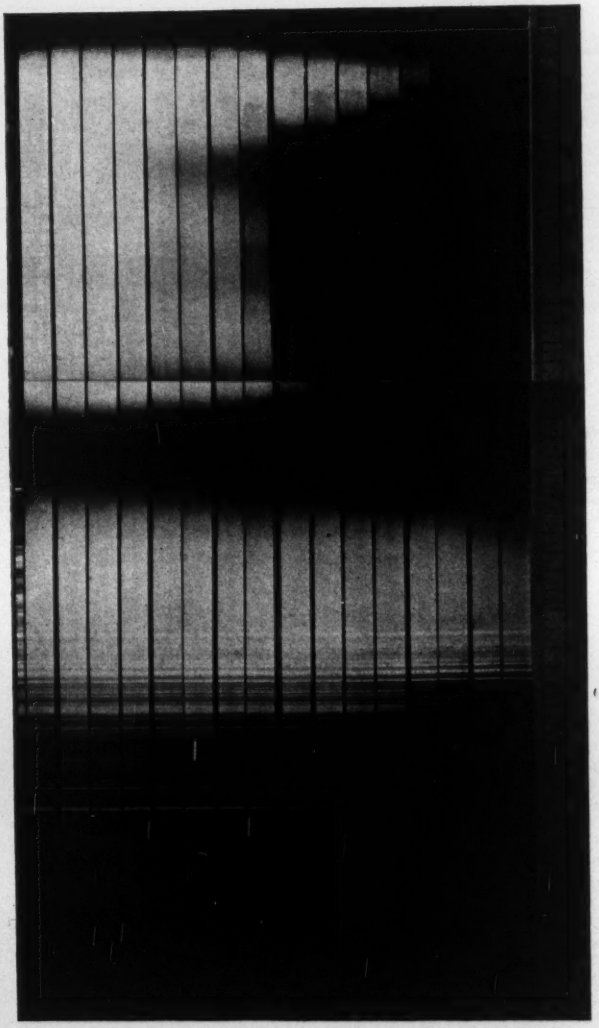
In B the absorption in this region of the spectrum is less intense, especially for the more dilute solutions, which show faint transmission throughout the band. The red edge of the band for the most concentrated solution is at λ 6970, while for the most dilute solution it is at λ 6800; the wave lengths given correspond to the limits of transmission, as indicated by the photographic blackening of the negative. The strips for the more dilute solutions of set B show faint traces of bands, which appear to correspond approximately in position to the bands noted in the analogous solutions in methyl alcohol. The bands at λ 5910 and λ 6050 show only faintly, and they both appear much less clearly defined than in the methyl alcohol solutions.

Cobalt Chloride in Ethyl Alcohol to which Water is Added (*See Plate III.*).

The concentration of cobalt chloride throughout was 0.088. The percentages of water, beginning with the solution used in making the strip nearest the numbered scale, were 0, 1, 2, 3, 4, 5, 5.5, 6, 6.5, 7, 7.5, 8, 9, 10, 11, and 12. The duration of the exposures to the Nernst lamp and the spark was $1^1/_8$ and 3 minutes, respectively; the slit was adjusted to a width of 0.01 cm. The common depth of absorbing layer was 2.0 cm.

In the four solutions containing the least amount of water the bands at λ 3100 and λ 3600 are very intense, making the absorption for the solution in pure ethyl alcohol complete from λ 3800 to the end of the ultraviolet. The bands, how-

Plate III.



ever, disappear rapidly on addition of water, so that in the strip corresponding to 6 per cent of water they can hardly be noticed. This strip transmits light as far out at λ 2600, while on the strip 10r the solution containing 12 per cent of water transmission extends to λ 2475.

The band in the green behaves very much the same as it does in methyl alcohol, being, however, somewhat fainter in ethyl than in methyl alcohol. Its middle for the solution containing 12 per cent water is at λ 5200. For the solution in pure ethyl alcohol it is not possible to determine its middle, as it unites with the strong absorption band in the orange and red, this solution showing complete absorption from about λ 4930 to λ 7200.

The absorption band in the red narrows very rapidly with addition of water. Its limits for the solution containing 3 per cent of water are λ 5750 and λ 7000. In the strips corresponding to the solutions containing from 5 to 7.5 per cent of water, the band breaks up into a rather complicated spectrum. Absorption bands may be noticed having centers at λ 5910, λ 6060, λ 6240, λ 6400, and λ 6700. Of these, the last is the strongest and widest. The one at λ 6400 is very faint, the one at λ 5910 a little more intense; while those at λ 6060 and λ 6240 are fairly intense, comparing favorably with the bands in the same region seen in the corresponding methyl alcohol solution.

Referring to the description of the negatives from which Plate II. was made, it will be recalled that, although the absorption in the red showed signs of breaking up into finer bands, these did not appear very distinctly. Indeed, the only ones that could be made out were those at λ 5910 and λ 6060. The water added to solutions of cobalt chloride in ethyl alcohol must hence play an important part in the development of these bands, and it is barely possible that the faint development of the bands noted in Plate II. may have been due to the slight traces of water which it is impossible to remove from ethyl alcohol, or which might have found its way into it in the process of pouring the solution into the cell and exposing this in the spectrograph. It is probable that the ac-

tivity of water in producing changes in the absorption spectrum depends not upon the percentage relation of water to alcohol, but upon that of water to amount of salt in a given volume of the solution. This was found to be so for solutions of neodymium salts in mixed solvents, which will be discussed in the section dealing with the rare earths. If this rule also applies to cobalt salts, we may say that since 5 per cent of water produces a fair development of the bands in a solution of concentration 0.088, it would require only about 1 per cent of water to do the same in the most dilute solution used in making the negative for Plate II., the concentration of which was 0.02. The bands there were much less clearly developed, which, if they were caused by water, would indicate the presence of water to an amount of about 0.5 per cent, which is well within the range of probability.

It is not at all improbable that the absorption bands in the red region of the spectrum, shown by solutions of cobalt salts dissolved in ethyl alcohol, may be used as a delicate test for the presence of water in the solvent.

General Summary of Results with Cobalt Salts.

We shall consider the aqueous solutions first, since they are the simplest from the standpoint of the absorption spectra. With two exceptions, all of the solutions studied at room temperatures and with such depths of absorbing layer as were employed, show only two regions of absorption, one in the ultraviolet and one in the green. The exceptions, both of which show some absorption in the red, are the concentrated solutions of the sulphocyanate, and the solutions of cobalt bromide to which large amounts of calcium bromide had been added.

Let us first consider the absorption in the ultraviolet. Solutions of all the salts studied, except the sulphate, have a region of so-called one-sided absorption, which cuts off more or less of the ultraviolet end of the spectrum, depending upon the salt used. In all cases the band narrows with dilution when the conditions for Beer's law obtain, but tends to remain approximately of constant width when molecules are kept con-

stant. In the bromide and nitrate the band is constant with molecules constant. This indicates that the absorber which is responsible for this band is in every case the undissociated molecule, and to account for the deviations from constancy in the band when the number of absorbers is kept constant, we may assume that the molecules in concentrated solutions associate to some extent, and that their absorbing power is thereby increased; or we may assume that with increasing dilution they become more and more hydrated, and that this decreases their absorbing power. A choice between these two explanations cannot be made without a further study of the subject.

In addition to the one-sided ultraviolet band, cobalt chloride has a band at λ 3300, which disappears rapidly with dilution even when molecules remain constant. This band seems to increase in intensity very rapidly with rise in temperature. We cannot very reasonably ascribe this band to the undissociated molecules as such, since it not only narrows rapidly but entirely disappears when these are kept constant. To explain it we must look, therefore, either to association or to hydration. It may be remarked here that by association we do not mean simply a grouping together of similar particles, but also a grouping together of such parts as molecules and ions, or aggregates of molecules and ions, etc. The term association, therefore, includes the complex anions assumed to exist by Donnan and Bassett. Both association and hydration are known to diminish with rise in temperature (except in Donnan and Bassett's complex anions); with increasing concentration at a given temperature association is known to increase while hydration decreases. In a fairly dilute solution the amount of association is perhaps negligible. If we then assume that the λ 3300 band is due to some aggregate, this would explain its disappearance on dilution, since this process destroys the aggregate. But raising the temperature also destroys the aggregate without, however, causing the absorption band to disappear. The fact is that it becomes more intense as the temperature rises. It seems, therefore,

rather difficult to assume that it is due to aggregates, at least to aggregates which are not abnormal in their behavior.

If we assume that the band is due to some *relatively simple hydrate* the facts are at once accounted for, since with rise in temperature complex hydrates break down into simpler ones. Also with increase in dilution more and more complex hydrates are formed, which would also cause the band to disappear.

The green band appears in all aqueous solutions, although with various intensities and apparently in somewhat different positions. The change in position is inappreciable in the case of dilute solutions, and with concentrated solutions it depends entirely upon whether the band widens symmetrically or not. In general, it widens perhaps a trifle more towards the violet, especially at first. A very slight amount of general absorption will shift the apparent center of an unsymmetrical band, and this is perhaps the explanation of the slight variation in the position of the center of this band in concentrated solutions of different salts.

The intensity of the band, as indicated by its width on the photographic plate, is more interesting. For if it is due to the cobalt cation as such, it ought to have a greater intensity in solutions which are strongly dissociated than in slightly dissociated solutions, concentration and depth of layer being constant.

Our spectrograms of cobalt solutions show the following: For solutions having a concentration of 2 normal or more, the salts arranged in the order of increasing intensity of the green band are: nitrate, bromide, chloride, sulphocyanate. For dilute solutions (concentrations of about 0.1 or 0.2 normal) the order is: bromide, chloride, nitrate, sulphate, acetate, sulphocyanate. Arranged in the order of increasing dissociation the salts would be: acetate, sulphate, sulphocyanate, nitrate, chloride, bromide. This is just the opposite of the order of increasing intensity of the green band, if we leave out the sulphocyanate. It is very evident, therefore, that something besides the cobalt cation must play a part in the production of this band.

It has been shown that when the concentration of the sulphate is varied from 0.65 to 0.06 the width of the band does not vary, provided the light is made to pass through such depths of the solution that the products of concentration and depth remain constant; it follows, therefore, that in this case the absorption is simply proportional to the number of cobalt atoms in the solution, and independent of whether these exist as ions, or combined with SO_4, as molecules, or as parts of the various aggregates or hydrates that we may assume to exist in the solution. The same is approximately true for the nitrate solutions, although in this case there is a slight narrowing of the band, indicating that the absorbing power of the various "absorbers" is not the same. In general, the simplest explanation of the green band is to assume, as we have just done, that the cobalt atom, no matter what it is combined with, has the power of absorbing green light, the intensity of the absorption depending, however, upon the nature of the combination.

Aqueous solutions show little or no absorption in the red unless they are very concentrated, or are at a high temperature, or relatively large amounts of such substances as hydrochloric acid, calcium chloride, or aluminium chloride, etc., are added to them. Whether the absorption produced by these different methods is the same or not for any given salt cannot yet be answered definitely. We have pointed out that the absorption of a solution of cobalt bromide to which a large amount of calcium bromide is added is similar *but not identical* with that of a solution of the chloride of cobalt to which a large amount of calcium chloride had been added. The work of Jones and Uhler ("Hydrates in Aqueous Solution") indicates that the absorption of cobalt chloride, when "dehydrated" with calcium chloride, aluminium chloride, or calcium bromide, is the same, but that this differs somewhat from the absorption of very concentrated solutions of cobalt chloride alone. In the latter case only three of the five bands were seen, and these were located nearer the red end of the spectrum, but the "displacement" was different for different bands, amounting to 170 A. U. for the least refrangible, and to 115 A. U. for the most refrangible.

The entire absence of this red absorption in solutions of moderate concentration shows at once that it cannot be accounted for by the simple theory of dissociation, according to which there should be present only ions and molecules. The fact that the absorption does appear in *very* concentrated solutions naturally suggests that it may be due to aggregates of molecules, but this view is not tenable since the absorption increases with rise in temperature. The most reasonable explanation, and the one that best fits the facts, is that it is due to some relatively simple hydrate of the molecule. The conditions which favor the formation of a "simple" hydrate are high temperature, or great concentration, or the addition of large amounts of some dehydrating agent to a moderately concentrated solution, and in all of these cases the absorption in the red appears. That this explanation is the correct one is also made probable by the work of Russell on the absorption of the various dry salts of cobalt. The anhydrous salts also show absorption in the red, as do also the simple hydrates, while hydrates containing 6 molecules of water exert no absorption in this region of the spectrum.

In nonaqueous solvents only the chloride and bromide have been studied. The chloride, which in aqueous solutions showed an absorption band near λ 3300, has in the alcoholic solutions two bands, one at λ 3100 and the other at λ 3600. These bands behave very much like the λ 3300 band in the aqueous solution, disappearing quite rapidly with dilution. They are most likely due to some relatively simple solvate. A study of the change of absorption with temperature will undoubtedly throw some light on this point.

The green band is present in all the nonaqueous solutions studied, although its intensity in the acetone solutions is so small that very deep layers of solution were necessary in order to make even a trace of it visible. This is exactly what we should expect if the cobalt atom, no matter with what it is associated, absorbs green light to some extent. The intensity of the band diminishes as we pass from solutions in methyl alcohol to those in ethyl alcohol and acetone, but so do the concentrations; hence, as in aqueous solutions, the intensity

of the band may be said to be approximately proportional to the concentration.

In the red the absorption is much more intense in the non-aqueous than in aqueous solutions, the intensity for equal concentrations increasing very rapidly as we pass from methyl alcohol to ethyl alcohol to acetone. The structure of the band differs materially in the different solvents, as has been pointed out in the description of the spectrograms. With dilution it narrows rapidly in methyl alcohol, more slowly in ethyl alcohol, and remains constant or nearly so in acetone. That these changes cannot be explained by dissociation has already been pointed out by Jones and Uhler, who suggest that they may be due to *solvation*. This is altogether reasonable, and the behavior of the spectrum is exactly what we should expect from the conclusions reached in the discussion of aqueous solutions. The red absorption then was ascribed to "simple" hydrates, such as contain 2 or 3 molecules of water or less. It is not unlikely that "simple" solvates of cobalt salts, in general, have this property of absorbing red light.

We should expect the power to form solvates to be greater for methyl alcohol than for ethyl alcohol, and greater for the latter than for acetone. Hence, in the case of ethyl alcohol and acetone at ordinary temperature, all the solvates formed are perhaps simple enough to exert powerful red absorption, while with methyl alcohol this is true only with concentrated solutions or at elevated temperatures. The differences in the structure of the band in the different solvents are, of course, to be expected, since the "absorbers" are different.

SALTS OF NICKEL.

Among the more important investigations on the absorption spectra of nickel salts are the following:

Brewster,[1] in his early work on absorption, included the nitrate of nickel, and Emsmann[2] also studied the same salt.

Vogel[3] studied not only cobalt chloride but also the chloride of nickel, in connection with its power to absorb light.

[1] Phil. Mag. [4], **24**, 441 (1862).
[2] Pogg. Ann., Erganzb., **6**, 334 (1875).
[3] Ber. d. chem. Ges., **8**, 1533 (1875).

The work of Soret,[1] in 1878, also had to do with the chloride of nickel.

The splendid investigations of Hartley[2] on absorption spectra included also certain salts of nickel.

The work of Müller[3] in connection with salts of nickel calls for special comment. He tested Beer's law for certain salts of nickel and copper, and found that it holds for the sulphate and nitrate of nickel. The chloride and bromide of nickel showed deviations from the law. These deviations are to be explained, he thinks, on the basis of dissociation.

In a subsequent paper Müller[4] tests the above suggestion, and comes to the conclusion that dissociation alone cannot account for all the deviations from Beer's law. If the law does not hold, rise in temperature would produce a change in the absorption, and this would be similar to the effect produced by increase in concentration.

The fact is that rise in temperature produces effects on absorption different from those caused by increase in concentration, which shows that more than one factor must be taken into account in dealing with the causes of the deviation from Beer's law.

Müller thinks that both hydration and molecular complexes come into play.

It was thought neither necessary nor desirable to study the salts of nickel as exhaustively as those of cobalt. Several plates were, however, made, under the following conditions: Nickel chloride in water—Beer's law; nickel chloride in water—ions constant; nickel chloride in water—molecules constant; nickel chloride in water with calcium and aluminium chlorides; nickel sulphate in water—Beer's law; nickel acetate in water—Beer's law.

Only two of the nickel plates are given: Nickel chloride in water—Beer's law; and nickel chloride in water—molecules constant.

[1] Arch. Sci. Phys. Nat., **61**, 322 (1878).
[2] Trans. Roy. Dub. Soc. [2], **7**, 253 (1900); J. Chem. Soc., **83**, 221 (1903).
[3] Ann. Phys., **12**, 767 (1903).
[4] *Ibid.*, **21**, 515 (1906).

Plate IV.

A B

Nickel Chloride in Water—Beer's Law (See Plate IV.).

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 2.66, 2.00, 1.33, 0.89, 0.61, 0.44, and 0.33, the corresponding depths of layer being 3, 4, 6, 9, 13, 18, and 24 mm. For B the concentrations were 0.44, 0.33, 0.22, 0.15, 0.101, 0.073, and 0.055; the depth of layers were the same as for A.

The solutions were green, the more dilute ones tending towards a light yellowish-green. The exposures to the Nernst lamp and spark were $1^1/_6$ and 3 minutes, respectively, the slit having a width of 0.01 cm.

Plate IV., A, shows three regions of absorption, one in the extreme ultraviolet, a band in the end of the visible violet, and a band cutting off the extreme red. Besides this there is a rather strong general absorption in the entire ultraviolet beyond the absorption band in the end of the violet.

The extreme ultraviolet absorption perhaps narrows slightly with dilution, although from the second strip to the seventh the limit of transmission seems to remain almost fixed at λ 2550. The first solution, however, shows much more absorption in the whole ultraviolet region, including the band at λ 3960.

The band at λ 3960 narrows from the first to the third strips (counting from the scale) and then remains of constant width, the limits of transmission being approximately λ 3700 and λ 4230. The scale in the reproduction is shifted towards the red by nearly 50 A. U., due to the fact that in making the prints this was adjusted with reference to the narrow comparison strip seen at the top of the spectrogram. This strip is displaced, as may be seen by comparing the spark lines in the ultraviolet. The scale for the red end of the plate is, however, correctly placed, so that there is a slight discrepancy at the point where the two prints were joined together.

The absorption in the red shades off very gradually through a range of wave lengths of about 1000 A. U., being quite noticeable on the negative at λ 6100 in the strip corresponding to the most concentrated solution, and at λ 6200 in the strip

corresponding to the most dilute solution. The limits of transmission for the two strips are at λ 7150 and λ 7250, respectively. These measurements indicate a slight narrowing of the absorption band with dilution, but it must be remembered that photographic registration of the spectra is not the best method for studying such very hazy absorption bands, since a very slight change in the length of exposure or in the intensity of the source of light used may apparently shift the band very markedly. The only satisfactory method for studying such cases of hazy absorption is a spectrophotometric determination of the absorption coefficient for a number of wave lengths in the region.

In B the absorption in the extreme ultraviolet has disappeared, the last lines in the spark showing as well in the strips taken through the solutions as in the narrow comparison strip where there was nothing but air in the path of the beam of light.

The band at λ 3960 has become faint, but still shows distinctly on the negative. It remains unchanged in intensity in the seven strips on the spectrogram.

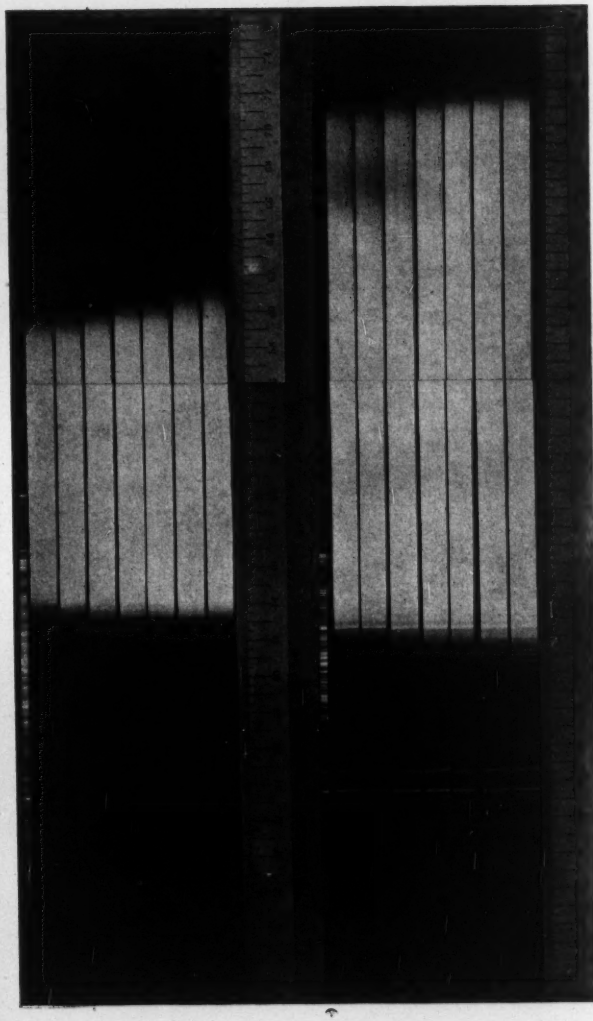
The absorption in the red, although present, as shown by the green color of the solutions in their bottles, was of too diffuse a character to be registered on the photographic plate, which, hence, shows complete transmission to beyond λ 7400. On the whole, except for the most concentrated solution, Beer's law seems to hold quite accurately for nickel chloride.

Nickel Chloride in Water—Molecules Constant (*See Plate V.*).

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 2.66, 2.18, 1.63, 1.22, 0.935, 0.750, and 0.610; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm. For set B the concentrations were 0.800, 0.660, 0.493, 0.365, 0.280, 0.220, and 0.160; the depths of the cell were the same as for set A. The exposures to the Nernst lamp and spark were 1 and 3 minutes, respectively, the slit having a width of 0.01 cm.

The general ultraviolet absorption beyond the λ 3960 band

Plate V.



A B

seems to remain nearly constant in the five most concentrated solutions of set A, then increases markedly in the sixth and seventh. The λ 3960 band narrows slightly from the first to the second strip (counting from the scale), then begins to widen, slowly at first, but more rapidly from the fifth to the seventh solutions.

In B the general ultraviolet absorption may still be seen, and it increases with dilution. The λ 3960 band also widens regularly with dilution. In the red the absorption increases regularly with dilution in both A and B.

The absorption bands of nickel salts seem to be very similar in their behavior to the green band of cobalt. In our study of that band we came to the conclusion that the power of absorption for green light is a property of the cobalt atom, and is only slightly affected by its immediate surroundings. Similarly, it appears from our study of nickel salts that the absorption shown by them is a property of the nickel atom, and there are only a few indications that it is changed very much by the immediate surroundings.

One of these is the marked widening of the λ 3960 band in nickel chloride as we approach a saturated solution. Others are the widening of the same band when large quantities of calcium or aluminium chlorides are added, and the appearance of the narrower bands in the orange and red, together with the change in the general absorption there under the same conditions. These point to the fact that the absorption of the simplest hydrates is somewhat different from that of the more complex ones, all of which (if there are several) seem to have about the same action on light. More definite conclusions on this subject must be deferred until the investigation shall have been extended to more compounds and under more varied conditions.

SALTS OF COPPER.

A number of investigators have included salts of copper among those whose absorption spectra they have studied. The results obtained with copper salts are, however, neither as interesting, nor apparently as important, as those furnished by cobalt, for example.

Hartley[1] included the chloride and bromide of copper in his elaborate investigations on absorption spectra; and Müller,[2] in his discussion of the deviations from Beer's law, dealt with the salts of both copper and nickel. Hartley explained the color changes in the case of copper chloride on addition of water as due to the formation of the compounds $CuCl_2.H_2O$ and $CuCl_2.2H_2O$ from the compound $CuCl_2$.

Donnan and Bassett,[3] in their interesting paper in which they develop the conception of complex ions as the cause of certain color changes in solution, also include cupric chloride.

Knoblauch[4] also studied the absorption spectra of copper sulphate.

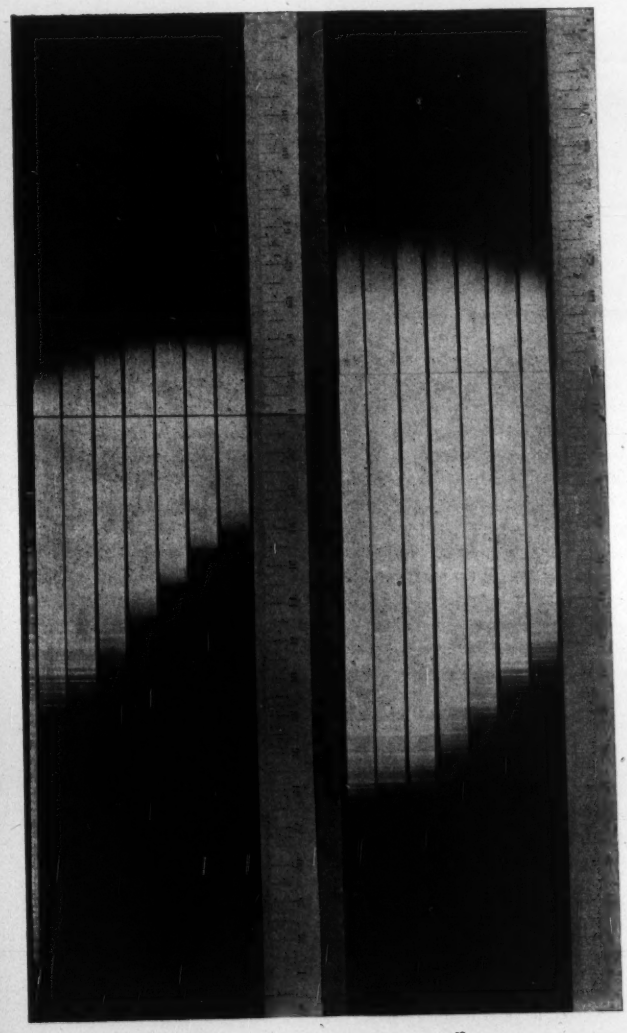
A number of salts of copper were studied pretty thoroughly in the present connection. These include copper chloride in water—Beer's law; copper chloride in water—molecules constant; copper chloride in methyl alcohol—Beer's law; copper chloride in ethyl alcohol—Beer's law; copper chloride in acetone —Beer's law; copper chloride in methyl alcohol with water; copper chloride in ethyl alcohol with water; copper chloride in acetone with water; copper bromide in water—Beer's law; copper bromide in water—molecules constant; copper bromide in methyl alcohol—Beer's law; copper bromide in ethyl alcohol—Beer's law; copper bromide in methyl alcohol and water; copper bromide in ethyl alcohol and water; copper intrate in water—Beer's law; copper nitrate in water—molecules constant. Only three of the copper plates are given in this paper.

Copper Chloride in Water—Beer's Law (*See Plate VI.*).

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 4.5, 3.37, 2.25, 1.50, 1.038, 0.750, and 0.562; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm. For B the concentrations were 1.5, 1.12, 0.75, 0.50, 0.37, 0.25, and 0.19; the depths of cell were the same as in A. The concentrated solutions, as

[1] Trans. Roy. Dub. Soc. [2], **7**, 253 (1900).
[2] Ann. Phys., **12**, 767 (1903).
[3] J. Chem. Soc., **81**, 955 (1902).
[4] Wied Ann., **43**, 738 (1891).

Plate VI.



viewed in their bottles, were green. With dilution, the color changed through greenish-blue to a rather light blue. The exposures to the Nernst lamp and spark were $1^1/_3$ and 3 minutes, respectively, the slit having a width of 0.01 cm.

The spectrogram shows two regions of absorption, one in the blue, violet, and ultraviolet, and the other in the red. The two are evidently of quite different character, since the former narrows very rapidly with decrease in concentration, the other only slightly.

In A the first strip shows that transmission ends at λ 4750, while for the seventh strip the limit is at λ 3750. The change in absorption is most rapid from the second to the fifth strips, giving the edge of the band the form of a compound curve. In B the band narrows most rapidly from the first to the fourth strips, the corresponding limits of transmission being λ 3950 and λ 3400. In the seventh strip transmission ceases at λ 3250.

The edge of this ultraviolet band is fairly well-defined throughout, differing in this respect from that of the red band, which is somewhat hazy, although much less so than was the case with the red band of nickel.

In the red the first strip of A shows complete absorption from λ 5900 to the end of the spectrum. The seventh strip shows transmission as far as λ 6150. The corresponding readings for the first and seventh strips of B are λ 6450 and λ 6675. The edge is, however, very indefinitely defined in B, the shading being considerable.

It appears, therefore, that the red band also narrows with dilution, although much less than the ultraviolet one. It also narrows more rapidly at first, giving the edge of the band a curved form, concave towards shorter wave lengths. At great dilutions and correspondingly deep layers of solution, the edge of the band would in all probability be straight, and perpendicular to the length of the strips.

Copper Chloride in Water—Molecules Constant (*See Plate VII.*).

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 4.53, 3.59, 2.63, 1.97, 1.50,

1.19, and 0.97; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm. For B the concentrations were 1.50, 1.22, 0.91, 0.68, 0.52, 0.415, and 0.335; the depths of cell were the same as for A. The exposures to the light of the Nernst lamp and spark lasted 1½ and 3 minutes, respectively, the width of the slit being 0.01 cm.

In this spectrogram we find that the absorption band in the ultraviolet still narrows rapidly, while that in the red shows a tendency to widen with dilution. The limits of transmission shown by the first and seventh strips of A are λ 4750 and λ 4100, with the edge showing a compound curve similar to the one in Plate VI., A, but with less curvature. For the first and seventh strips of B the limits are λ 3990 and λ 3500, the edge forming a curved line convex towards the region of short wave lengths. In the red, the first strip of A gives the limit of transmission as λ 6050. In the second and third strip the limit is a little farther up in the red, being near λ 6075. In the fourth strip it is again at λ 6050, from which it moves gradually towards shorter wave lengths until the seventh strip is reached, where it is at λ 5975. The edge of the band is hence curved, with the convex side towards the longer wave lengths.

In B the band widens continuously with decreasing concentration, the limit of transmission for the solution corresponding to the first strip being λ 6500, while the seventh strip shows complete absorption at λ 6400. The edge is not sharply defined, the shading extending as far as λ 5000 with considerable intensity. From λ 6000 to λ 5950 the blackening of the negative increases very rapidly, and this position of most rapid increase in transmission seems to be sensibly the same for all the solutions of the one series. This is also nearly the position of the limit of transmission for the concentrated solutions used in A, and also in Plate VI., A. Hence, it seems likely that this is the real limit of the absorption band.

Copper Chloride in Methyl Alcohol—Beer's Law (*See Plate VIII.*).

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.744, 0.595, 0.469, 0.372,

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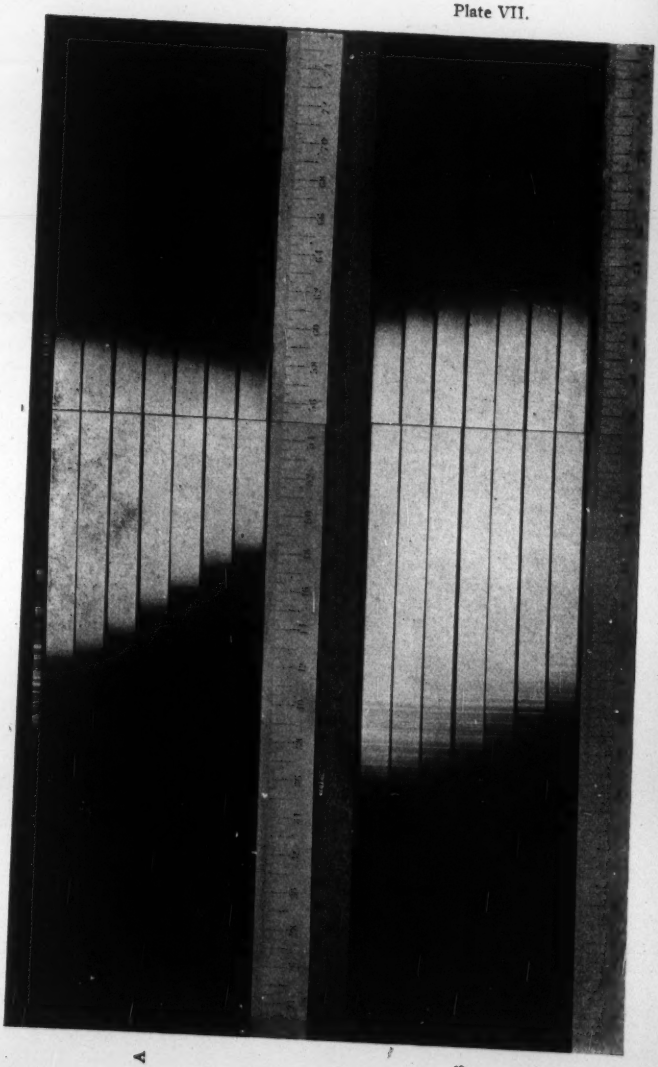
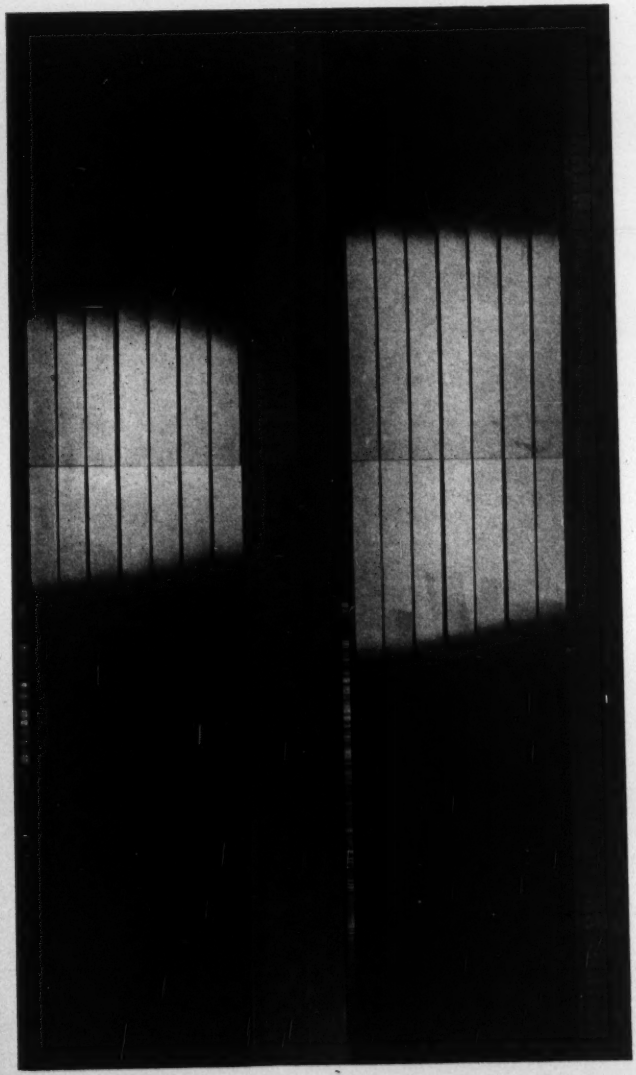
Plate VII.



A B

Plate VIII.



A B

0.297, 0.233, and 0.186; the corresponding depths of absorbing layer were 6, 7.5, 9.5, 12, 15, 19, and 24 mm. For B the concentrations were 0.233, 0.186, 0.147, 0.116, 0.093, 0.073, and 0.058; the depths of absorbing layer were the same as in set A.

The solutions were all green, only the intensity of the color changing with dilution. Exposures to the light of the Nernst lamp and spark lasted for 1½ and 3 minutes, respectively, the slit having the usual width of 0.01 cm.

As in the aqueous solutions we have two regions of absorption, one in the blue, violet, and ultraviolet, the other in the red. Both regions contract somewhat when the concentration of the solutions is decreased, but the one in the violet region contracts much more than the one in the red.

The limit of transmission for the first strip in A is at λ 4800, while for the seventh strip it is at λ 4630. The edge of the band forms a line which is slightly curved at first, the concave side being towards the violet. From the third to the seventh strips the line formed by the edge is sensibly straight. In B the limit of transmission for the first strip is λ 4420, while for the seventh it is λ 4200, the edge forming a line which is very nearly straight. From the fourth to the seventh a slight curvature with the convex side towards the violet may be noted. On the whole, this band behaves exactly as it does in aqueous solution, the only difference being the greater deviation from Beer's law in the latter case.

In the red, the first strip in A shows transmission to λ 6500 with shading from λ 6050; the seventh strip, transmission to λ 6580, with shading from λ 6100. The first strip in B shows transmission to λ 6950, shading perceptibly from λ 6550, while the seventh strip shows transmission as far as λ 7020, with shading from λ 6600. In both sets, therefore, the band narrows slightly with dilution, and in B quite uniformly with the decrease of concentration. In A, however, the narrowing is considerably more rapid at first. Here, again, we find that the band behaves in a manner very similar to what we found in the aqueous solution, only the change is somewhat slower. The decrease in concentration from strip to strip here, however, is only about half what it was in the aqueous solution; and

taking this into consideration the difference is not as great as it seems at first glance.

In general, the absorption spectrum of copper salts in the region of the spectrum investigated is much simpler than that of cobalt salts, inasmuch as it presents only two, or at most three, absorption bands. Of these, only the one at λ 4730 in acetone solutions lies wholly in the spectral region studied; the band in the ultraviolet is what might be termed one-sided, no region of transparency on its more refrangible side having ever been found. The band in the red is, however, strictly a band, a region of transparency existing in the infra-red. The behavior of this band throughout strongly suggests the green band of cobalt salts in solution, while the ultraviolet absorption is somewhat different from anything we have found thus far, resembling more nearly the absorption of iron salts, to be discussed in the next section.

Since the absorption in the ultraviolet decreases rapidly with dilution, when the product of concentration and depth of layer is kept constant, it seems reasonable to suppose that the copper ion has little or nothing to do with it, and hence that it must be ascribed to the molecules; but as the absorption decreases with dilution, even when molecules are kept constant, without, however, entirely disappearing (as was the case with some cobalt bands), we must conclude that the absorbing power of a molecule is influenced considerably by its immediate surroundings. As usual, there are at least two possible ways of explaining the increase in the absorption with concentration when molecules are kept constant. One is to assume the formation of aggregates of molecules, and that the absorbing power of the molecule is increased thereby; the other is to assume the existence of solvates, and that the absorbing power of a molecule decreases with increase in the complexity of the solvate. To decide between these two possible explanations we need only take into account the change in the absorption produced by a rise in the temperature of the solution. This change is the same qualitatively as that produced by increasing the concentration. Molecular aggregates are broken down by rise in temperature, and hence, according to the assumption

made above as to the effect of aggregates on absorption, this should *decrease* the absorption instead of *increase* it. We must conclude, therefore, that the change in the absorption is not due to the formation of aggregates.

Solvates are made simpler both by increasing concentration and by rise in temperature, and, accordingly, from the assumption stated above regarding the effect of complexity of solvates on absorption, both changes should produce similar differences in the absorption spectrum. This is in accordance with observed facts. We conclude, therefore, that the ultraviolet absorption of solutions of copper salts is due to the "solvated" molecules of the dissolved salt, and that the absorbing power of such molecules is decreased as the complexity of the solvate increases.

It will be remembered that for equal concentrations the absorption in the region of shorter wave lengths is least in the aqueous solutions, then increases as we pass from methyl alcohol to ethyl alcohol. In general, also, it may be stated that the change in the absorption with dilution is greatest for the aqueous solution, and then decreases as we pass to methyl and ethyl alcohol. This is just what we should expect, since the power to form solvates is greater for water than for either of the alcohols, and greater for methyl than for ethyl alcohol; hence, in solutions of equal concentration the solvates should decrease in complexity when we pass in the direction—water, methyl alcohol, ethyl alcohol. Also the change in the complexity of the solvate, on dilution, should be greater in the water solutions than in the methyl or ethyl alcohol solutions.

The absorption band in the red narrows somewhat when the product of concentration and depth of absorbing layer is kept constant, but widens when molecules are kept constant. Its intensity does not change nearly as much as that of the violet band when the solvent is changed, the concentration being the chief factor which determines it. Hence we conclude that this band, like the green band of cobalt salts, is due to the metallic atom, and that its absorbing power is affected only slightly by its immediate surroundings. The peculiar behavior of the red band of copper chloride in methyl alcohol,

on addition of water, is interesting, especially as its explanation is not at all difficult, although it may not at first seem so simple. It will be recalled that here the band first widened when water was added, and then, as the amount of water was increased, it narrowed regularly. Now, when a small amount of water is added it is reasonable to conclude that the hydrates formed would be comparatively simple, and that as the amount of water is increased their complexity increases also.

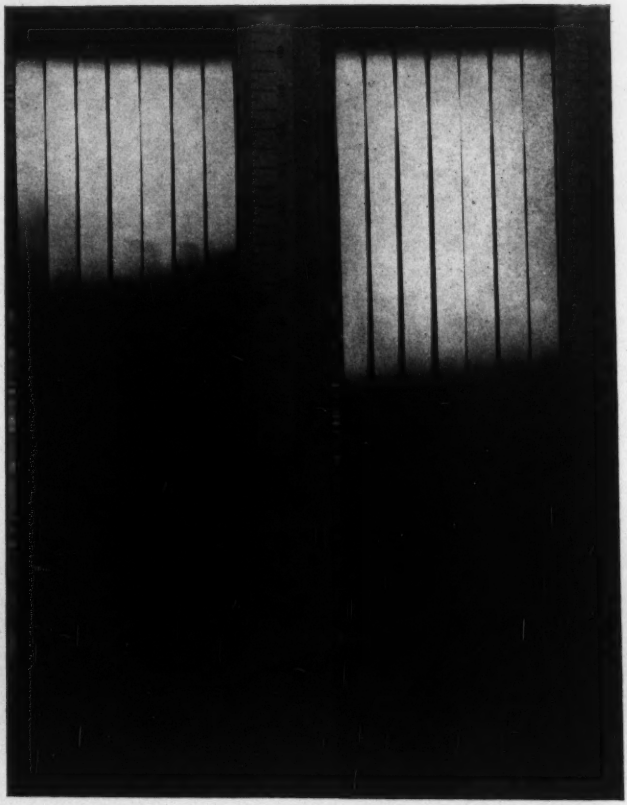
We have stated that the effect of the surroundings on the absorption of the copper atom for this region of the spectrum is slight compared with what it is in the ultraviolet; but that it is quite appreciable is shown by the narrowing of the band wherever the conditions for Beer's law hold. We believe that this narrowing is due to a change in the complexity of the solvates. To explain the case in question, then, we need only say that the absorption of the comparatively simple hydrates formed when a small amount of water is added is greater than that of the methyl alcoholates already existing in the original solution; and that, therefore, the first effect observed is a widening of the band. Its subsequent narrowing as more water is added is, of course, due to the increase in the complexity of the hydrates.

In the similar solutions in ethyl alcohol the band narrowed from the very first, which is just what we should expect, since the solvates here are simpler than in methyl alcohol and hence their absorbing power would be equal to, or greater than, that of the simple hydrates first formed.

SALTS OF IRON.

A few salts of iron were studied under a few conditions. Thus: Ferric chloride in water—Beer's law; ferric chloride in water—molecules constant; ferric chloride with calcium chloride; ferric chloride with aluminium chloride; ferric chloride in methyl alcohol—Beer's law; ferric chloride in ethyl alcohol—Beer's law; ferric chloride in acetone—Beer's law. Only one iron plate is given, since the results obtained with salts of this metal are less interesting and less important than those with any other element.

Plate IX.



A B

Ferric Chloride in Water—Beer's Law (See Plate IX.).

The concentrations of the solutions used in making the negative for A, Plate IX., beginning with the one whose spectrum is adjacent to the numbered scale, were 1.30, 0.97, 0.65, 0.43, 0.30, 0.22, and 0.16; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm. For B, Plate IX., the concentrations were 0.22, 0.16, 0.11, 0.073, 0.051, 0.037, and 0.027; the depths of cell in both cases were the same as for A.

The most concentrated solutions, as viewed in their bottles, were reddish-orange, changing through orange-yellow to nearly colorless in the last members of the third series. The exposure to the light of the Nernst lamp lasted for 1 minute, the slit having a width of 0.01 cm. No exposure to the light from the spark was made, as it was ascertained by a preliminary trial that even the most dilute solution was opaque in the entire ultraviolet beyond λ 3600. A trial also showed complete transmission in the red as far as λ 7400, and hence no red-sensitive plates were used. Therefore, all the spectra of iron salts shown in this section seem to end at λ 6000 or near there, which simply shows that the Seed film used was not sensitive to light of longer wave length than about λ 6000.

The absorption decreases fairly regularly with dilution, the decrease being, however, less at high dilutions. The limits of transmission for the most concentrated and most dilute solutions of each of the three sets are λ 4850 to λ 4600, λ 4220 to λ 4100, and λ 3900 to λ 3800, respectively, the narrowing of the band in the first set amounting to 250 A. U., whereas, in the third set it was only 100 A. U.

An attempt was made to carry the dilution still farther, but it was found that the very dilute solutions changed color so rapidly with time that no confidence could be placed in the results obtained.

SALTS OF CHROMIUM.

A comparatively large number of investigators have worked on salts of chromium from the standpoint of absorption of light. We need only mention the work of Talbot,[1] Brewster,[2]

[1] Phil. Mag. [3], **4**, 112 (1834).

[2] Phil. Trans., **1835**, 1, 91; Phil. Mag. [4], **24**, 441 (1862).

Croft,[1] Müller,[2] Gladstone,[3] Melde,[4] the early work of Hartley,[5] Vierordt,[6] Vogel,[7] E. Wiedermann,[8] Soret,[9] Settegast,[10] Moissan,[11] Pulfrick,[12] Zimmermann,[13] Becquerel,[14] Liveing and Dewar,[15] Schunck,[16] Recoura,[17] and Sabatier.[18]

Knoblauch,[19] in his interesting and important investigation on the absorption spectra of very dilute solutions, studied a number of chromium compounds. These were the chloride, nitrate, sulphate, acetate, oxalate, potassium chrom-oxalate, and chrom-alum. Knoblauch directed a part of his work to testing the consequences of the then recently-proposed theory of electrolytic dissociation. According to this theory, the absorption spectrum of a concentrated solution must be different from that of a very dilute solution; and at dilutions of complete dissociation, all salts with colorless cations and a common colored anian, or salts with colorless anions and a colored cation must have the same absorption spectrum. Knoblauch found that neither of these conclusions from the theory were verified experimentally.

Ostwald[20] showed a little later that the second consequence of the theory is fully verified by experimental facts.

Knoblauch also tested Beer's law, and found that it held for many salts within wide limits of concentration. He concluded that the apparent deviations from the law are to be explained as due to chemical or physical changes in the solutions.

[1] Phil. Mag. [3], **21,** 197 (1842).
[2] Pogg. Ann., **72,** 76 (1847); **79,** 344 (1850).
[3] Phil. Mag. [4], **14,** 418 (1857); J. Chem. Soc., **10,** 79 (1858).
[4] Pogg. Ann., **124,** 91 (1865).
[5] P. Roy. Soc., **21,** 499 (1873).
[6] Ber. d. chem. Ges., **5,** 34 (1872).
[7] *Ibid.*, **11,** 913, 1363 (1878).
[8] Wied Ann., **5,** 500 (1878).
[9] Arch. Sci. Phys. Nat. [2], **61,** 322 (1878); [2], **63,** 89 (1878).
[10] Wied Ann., **7,** 244 (1879).
[11] Compt. rend., **93,** 1079 (1881).
[12] Z. Kryst., **6,** 142 (1882).
[13] Ann. Chem. (Liebig), **213,** 285 (1882).
[14] Ann. Chim. Phys. [5], **30,** 5 (1883).
[15] P. Roy. Soc., **35,** 71 (1883).
[16] Chem. News, **51,** 152 (1885).
[17] Compt. rend., **102,** 515 (1886); **112,** 1439 (1891).
[18] *Ibid.*, **103,** 49 (1886).
[19] Wied Ann., **43,** 738 (1891).
[20] Z. physik. Chem., **9,** 579 (1892).

Hartley,[1] in his elaborate investigations on absorption spectra, studied a number of salts of chromium. The salt $Cr(NO_3)_3.9H_2O$ is violet in color. When heated to 100° it changes to green. Hartley concludes that the violet are the normal salts of chromium, while the green are chromyl salts, thus:

	Violet salts.	Green salts.
Chloride	$CrCl_3.3H_2O$	$Cr_2OCl_4.2H_2O$
Sulphate	$Cr_2(SO_4)_3.15H_2O$	$Cr_2O(SO_4)_2.xH_2O$
Nitrate	$Cr_2(NO_3)_6.9H_2O$	$Cr_2O(NO_3)_4.H_2O$

An interesting paper by Vernon[2] on "The Dissociation of Electrolytes in Solution as Shown by Colorimetric Determinations" was published in sections in the *Chemical News*. Chromium plays in this work what might be termed the exceptional rôle, as is seen from the following conclusions drawn by the author:[3]

"Almost all the solutions of the thirty-five colored salts examined show considerable decrease in color effect on dilution, due in all probability to dissociation taking place. The only exceptions are certain chromium derivatives, the color of whose solutions on gradual dilution either remains constant or increases slightly. All solutions of salts, with the exception of those of certain chromium derivatives and perhaps of potassium permanganate, increase considerably in color effect on being heated."

Lapraik[4] has described a large number of empirical relations between the absorption spectra of compounds of chromium. Certain classes of chromium compounds were found to have the same absorption spectra in solution and in the solid state. The band λ 710 to λ 692 is present in all of the chromium compounds investigated, with the exception of potassium chromium cyanide. In certain compounds, however, the band is displaced somewhat from the above position.

The broad absorption in the green in the region of λ 550 to λ 650 is present in all chromium compounds, sometimes dis-

[1] Chem. News, **65,** 15 (1892); Trans. Roy. Soc. Dublin [2], **7,** 253 (1900).
[2] Chem. News, **66,** 104, 114, 141, and 152 (1892).
[3] *Ibid.*, **66,** 154 (1892).
[4] J. prakt. Chem., **47,** 305 (1893).

placed somewhat towards the red, in other compounds towards the blue, as referred to the above wave lengths.

Etard[1] studied the sulphate of chromium, chrome-alum, and violet chromium nitrate. He found a band in the red, which was characteristic of chromium salts, and which extended from 670 to 678. He concluded that the absorption spectra of chromium salts are due to the molecules.

The absorption bands produced by an element are displaced in position, or may cease to exist entirely, depending upon the nature of the whole molecule which is in solution, *i. e.*, upon the particular compound of the element studied.

Two salts of chromium have been brought within the scope of this investigation, and under the following conditions: Chromium chloride in water—Beer's law; chromium chloride in water—molecules constant; chromium chloride with calcium chloride and aluminium chloride; chromium nitrate in water—Beer's law; chromium nitrate in water—molecules constant. Only one chromium plate is given.

Chromium Chloride in Water—Beer's Law. (*See Plate X., A.*)

The concentrations of the solutions, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.53, 0.40, 0.26, 0.17, 0.12, 0.09, and 0.07; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm.

The exposures to the light of the Nernst lamp and spark lasted 1⅛ minutes and 3 minutes respectively, the slit having a width of 0.01 cm.

In deep layers the more concentrated solutions were red, while in shallow layers they were green. The dilute solutions, as seen in their bottles, appeared green.

The spectrogram shows three regions of absorption: One is located in the extreme ultraviolet, cutting off the part of the spectrum lying to the more refrangible side of λ 2840. Another absorption band is in the violet, its more refrangible limit being at λ 3900, and moderately well-defined, while the red edge, which is more hazy, is near λ 4450. A third band is located

[1] Compt. rend., **120**, 1057 (1895).

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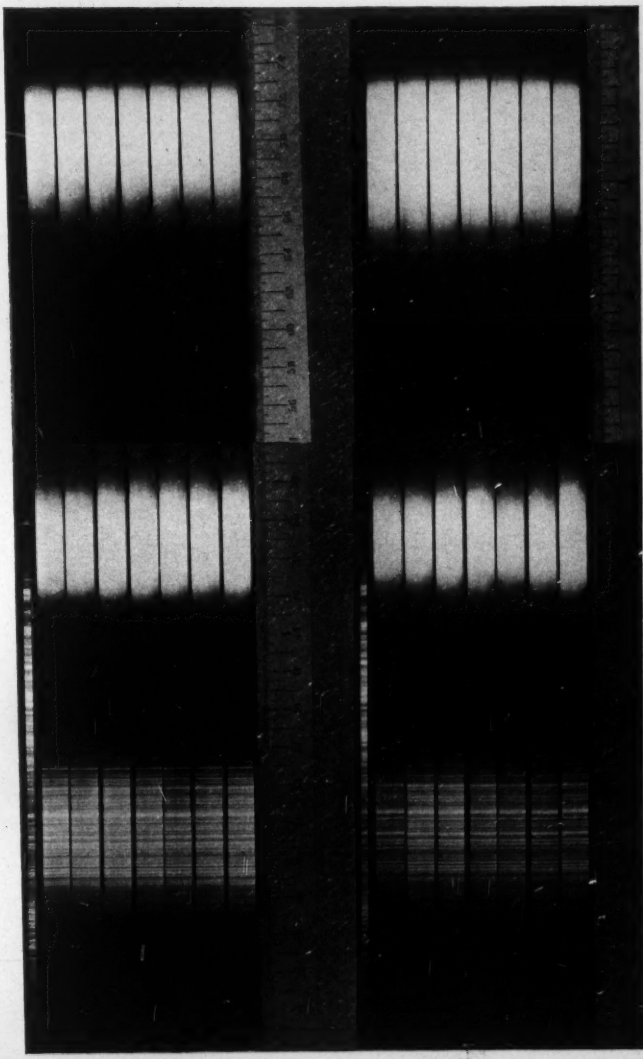
Plate X.



A B

in the yellow and orange. Both edges of this band are very diffuse, the red edge slightly more than the blue. The spectrograms indicate that the opposite is the case, but this is due to the fact that the blue edge of the band falls near the region or minimum sensibility of the Seed film, and, hence, the shading there is very much accentuated. The limits of transmission are at λ 5650 and about λ 6200, although there is considerable absorption as far "down" as λ 5200 and as far up as λ 6750. From λ 6800 to the end of the visible red the solutions are remarkably transparent. This was made very evident by the fact that a concentrated solution, about 20 cm. in depth, still transmitted red light freely, although not a trace of green could be seen through a layer 5 cm. deep.

The width of all these bands is absolutely unchanged by change in dilution, within the limits of concentration here used; hence the absorption is strictly proportional to the number of chromium atoms in the path of the beam of light, whether they exist as ions or combined with other atoms in a molecule.

Chromium Chloride in Water—Molecules Constant (*See Plate X., B.*).

The concentrations of the solutions, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.45, 0.35; 0.245, 0.173, 0.125, 0.093, and 0.074; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm. The exposures to the light of the Nernst lamp and spark lasted, 1⅛ and 3 minutes, respectively; the width of the slit was 0.01 cm.

The spectrogram shows the same regions of absorption as A, but in this case they all widen with decrease in concentration, as was to be expected. The bands all widen to nearly the same extent. The shading on the red side of the least refrangible band does not extend any farther into the red with decrease in concentration, this band having, therefore, a rather well-defined limit near λ 6800.

A rather narrow band of absorption may be seen at λ 6690.

It is faint and scarcely noticeable in A. Its width is not easily determined, but appears to be only about 30 A. U.

[*The remainder of this paper will appear in the April number of This Journal.*]

[Contributions from the Chemical Laboratory of the University of Texas.]

THE ELECTROMOTIVE FORCE OF NICKEL AND THE EFFECT OF OCCLUDED HYDROGEN.[1]

By E. P. Schoch.

The published accounts concerning the electromotive force of nickel are not only vague, but in the main conflicting. Neumann (1),[2] Siemens (2), and Euler (3) locate the potential of nickel in the neighborhood of 0.50 volt.[3] Other investigators (4) have not been able to satisfactorily duplicate this or any other value for the potential. More recently Muthmann and Fraunberger (5) placed the value of the potential Ni-N/1 $NiSO_4$ at 0.88 volt. They considered that the potential of "active" nickel is obtained only when passivizing influences are completely excluded. Hence they polarized nickel extensively with hydrogen in distilled water, then quickly transferred it to a N/1 nickel sulphate solution and observed the potential. In text-books (9) this high value has displaced the older determination of Neumann. However, the well-known fact that nickel occludes hydrogen, coupled with the results of Richards and Behr (10) on the effect of occluded hydrogen,[4] lead me to suspect that this high value is due, in part at least, to occluded hydrogen, and that it does not represent the reversible potential; and the following preliminary experiments showed me where the reversible potential is probably located.

[1] This and the following paper deal primarily with sulphate electrolytes.

[2] The numbers in parentheses refer to references given at the end of this paper.

[3] The potentials given in this paper are expressed in international volts. They refer to the normal calomel electrode as an arbitrary zero, and the values given are the observed values without any corrections. The measurements are made by the well-known Poggendorff compensation method with a capillary electrometer as a zero instrument.

[4] Richards and Behr located the potential of iron in N/1 ferrous sulphate solution at 0.71 volt, and showed that occluded hydrogen may produce much higher potentials. Muthmann and Fraunberger's value, obtained with iron polarized in distilled water and then transferred to N/1 ferrous sulphate solution, is 0.94 volt.

Nickel poles may show widely different potentials, depending upon their preparation, previous exposure, etc. Thus, nickel that has been lying in air will show in N/1 nickel sulphate solutions potentials ranging from 0.25 to 0.32 volt. Poles that have been prepared by boiling in sodium hydroxide solution and then dipping in concentrated hydrochloric acid showed 0.875 volt in the same electrolyte (N/1 nickel sulphate solution). Polarized anodically or cathodically in any liquid and then transferred to N/1 nickel sulphate solution, nickel poles will show almost any potential between 0.88 and zero or even lower. However, when nickel is allowed to remain in nickel sulphate solution free from air it attains a potential between 0.43 and 0.50 volt, irrespective of the potential which it showed just before. In N/1 sulphuric acid and in dilute hydrochloric acid, in both of which it dissolves slowly, nickel gives a potential of approximately 0.40 volt. At temperatures from 70° to 100° C., the metal attains approximately the same potential as at ordinary temperatures. At high temperatures nickel will attain this final potential very rapidly, while at ordinary temperatures more time is required.

These experiments indicate that the reversible potential of nickel is between 0.45 and 0.50 volt. A more accurate location of this potential is presented in the following pages.

The Potential of Nickel.

Since the lower potentials may be produced by air, it is necessary to remove and exclude this entirely, and for this purpose the liquids with the poles in them were boiled vigorously for several minutes and then cooled without allowing air to get into the apparatus, which was made as follows: A Bohemian flask, preferably one with a short, wide neck, is closed with a rubber stopper, through which is fitted the stem of the nickel pole and a glass syphon. The latter should terminate just at the lower surface of the stopper; the other end dips into another flask. The two flasks are clamped on a suitable stand; the stoppered flask is filled half full with the electrolyte and into the other flask is poured somewhat more of the electrolyte than would fill the first flask and the

tube, so that enough liquid will remain in the second flask to serve as a seal. The liquid in both flasks is boiled vigorously for several minutes. When the heat is withdrawn the condensation of the steam in the first flask will draw the liquid over from the second flask. In order to avoid a drawing over of solution saturated with air, which would occur if the large volume of liquid in the first flask were allowed to cool slowly, the stoppered flask is cooled rapidly by means of ice water. If the pole is to be kept for any length of time, mercury is poured into a second flask so as to serve as a seal to the glass tube.

The results indicate that oxygen or air may thus be almost completely removed. Any remaining portion of it will be so small as to lower the potential only 5 to 10 millivolts. Hydrogen cannot be removed nearly as completely; after boiling it may still be present in sufficient amount to raise the potential as much as 50 millivolts.[1]

The question of the neutrality of the solution had to be considered carefully. Not only do acidified solutions give a lower potential, but the merest trace of acidity is particularly effective. Thus, two samples of well-crystallized nickel sulphate (Merck) taken from the same lot gave potentials differing by 50 millivolts. The one which produced the lower potential was faintly acid to litmus; the other was neutral. I neutralized the remaining acidity of the first one with a slight excess of sodium hydroxide, filtered off the small amount of precipitate formed, and found that this liquid gave the same potential as the other neutral sample above. By this means I could get more closely agreeing results than I could without it, and since this was a step towards securing readily reproducible conditions, I have treated in the same way all solutions which are referred to as *neutral*.

The following results were obtained with neutral N/1 nickel sulphate solution, at ordinary temperatures (26° C.):

1. Commercial sheet nickel, 12–36 hours after preparation of pole, 0.47 volt.

[1] The effect of hydrogen, which raises the potential, is shown farther on in this paper, and that of oxygen, which lowers the potential, is discussed in the following paper on "The Behavior of the Nickel Anode."

2. Electrolytic nickel, Kahlbaum's, 12–36 hours after preparation of pole, 0.465 volt.

3. Electrolytic nickel, my own preparation, 12–36 hours after preparation of pole, 0.47 volt.

Nos. 1 and 3, after standing for six weeks, during which time the syphon was closed with a mercury seal, showed 0.48 volt, while another pole of commercial sheet nickel, after nine weeks, showed 0.487 volt.

Since the results obtained with commercial sheet nickel agree with those obtained with electrolytic nickel, only sheet nickel was used in the remaining experiments.[1]

A sample of commercial nickel was polarized cathodically and was then put into the flask, boiled, and cooled. It showed a potential of 0.55. After standing for six weeks it showed a potential of 0.485.

A nickel wire, No. 18 B & S gauge, was bent in the form of a spiral similar to the carbon filament in some of the electric lights. The ends were connected by clamps to two stout copper wires, which passed through the rubber stopper in a 500 cc. flask. This stopper was also fitted with two glass tubes by means of which the air in the flask was completely displaced by pure nitrogen. The nickel wire was heated to white heat in this gas. After allowing the flask to stand and cool, nickel sulphate solution which had been boiled and cooled under an atmosphere of nitrogen was introduced. Of course, only the nickel was allowed to dip into the electrolyte. This pole gave the following results:

At first, volt.	After 12 hrs., volt.	After 24 hrs., volt.	After 36 hrs., volt.
0.49	0.48	0.48	0.46

Since the solubility of the nickel anode is largely increased by hydrogen and halide ions, it is desirable to know if these ions affect the maximum electromotive force of nickel.

The potential of Ni–N/1 $NiCl_2$ at ordinary temperatures (26° C.) was found to be 0.42 volt—a result that may be con-

[1] The possibility that the potential may be due wholly or in part to a slight quantity of impurities in the metal is excluded by the fact that after extensive electrolytic corrosion the nickel shows the same potential as before. This was observed repeatedly in connection with the study of the behavior of the nickel anode.

sidered to be in accord with the potential of Ni-N/1 $NiSO_4$. Hence the potentials of nickel in nickel sulphate solutions which have only a relatively small amount of halide ions in them should not differ essentially from the potential obtained when the latter are absent.

I obtained the following results:

(1) An electrolyte 1/10 normal with potassium chloride, and 9/10 normal with nickel sulphate showed at first 0.46 volt; after 24 hours, 0.475 volt; after 36 hours, 0.475 volt.

(2) An electrolyte 1/10 normal with potassium fluoride and 9/10 normal with nickel sulphate showed, after 12 hours, 0.475 volt.

The effect of acidification was ascertained, with the following results:

1. An electrolyte 1/2500 normal with sulphuric acid and normal with nickel sulphate showed, for 12 hours, 0.455 volt.

2. An electrolyte which was 1/10 normal with sulphuric acid and normal with nickel sulphate showed, for 12 hours, 0.42 volt.

It is notable that neither halide nor hydrogen ions raise the potential. An explanation of the action of the acid in producing lower potentials is given on page 219.

The effect of increase in temperature appears to be to lower the potential. A nickel pole in neutral N/1 nickel sulphate solution which showed 0.47 volt at 26° gave in one case 0.42 volt at 95° C.; in other cases, 0.434 and 0.44 volt, respectively. A value higher than 0.44 volt was never observed.

The effect of concentration is most strikingly shown by using for an electrolyte a solution containing no nickel. Potassium or sodium sulphate serve equally well, provided they are both absolutely neutral. Normal potassium sulphate gave, after 12 hours, 0.56 volt at 26°. Since very dilute nickel sulphate appears to introduce difficulties into the measurement, I decided to use nickel sulphate with potassium sulphate in such concentrations that the sum of the normalities was always the same. I obtained the following results:

1. An electrolyte which is 1/100 normal with nickel sulphate and 99/100 normal with potassium sulphate gave, at

first, 0.53 volt, and, after 24 hours, 0.54 volt, where it remained constant for the next 24 hours.

2. An electrolyte which is 1/10 normal with nickel sulphate and 9/10 normal with potassium sulphate gave, at first, 0.50 volt, and, after 12 hours, 0.51 volt, where it remained constant.

It should be mentioned in this connection that there are indications of a reaction between nickel and potassium sulphate solution as a result of which a nickel-potassium alloy may be formed.[1] However, this appears to have no particular effect upon the potential, because nickel thus affected gives the usual potential in N/1 nickel sulphate solution.

Although the potassium sulphate employed in the foregoing experiments was strictly neutral to litmus, yet the question may be raised: Is the higher potential perhaps due to a lesser concentration of hydrogen ions in N/1 potassium sulphate than in N/1 nickel sulphate solution? Hence the following experiments were carried out:

1. Normal potassium sulphate which was also 1/2500 normal with potassium hydroxide gave:

At first, volt.	After 12 hrs., volt.	After 24 hrs., volt.	After 36 hrs., volt.
0.50	0.51	0.54	0.533

2. Normal potassium sulphate which was also 1/250 normal with potassium hydroxide gave, after 12 hours, 0.52 volt.

3. N/10 potassium hydroxide gave, after 12 hours, 0.52 volt.

4. N/1 potassium sulphate with N/2500 sulphuric acid showed, after 12 hours, 0.537 volt.

These results prove that the higher potentials shown by nickel in potassium sulphate solutions cannot be due to greater alkalinity or acidity of the solutions, because *both* lower the potential. Altogether we may safely conclude that the higher potentials are due to the difference in the concentrations of the nickel ions, and thus we have secured one of the most reliable indications of a reversible potential.

From the preceding data I have selected the value 0.48

[1] See page 244 of the following paper on "The Behavior of the Nickel Anode."

volt for the potential Ni–N/1 $NiSO_4$. This may be considered to be correct to within ± 5 millivolts. A nickel pole, which within 12 hours will approach this value—being at most 5 to 10 millivolts too low—can be prepared by using commercial nickel, or electrolytic nickel which has been exposed to the air long enough to allow all the hydrogen to escape. The electrolyte should be absolutely neutral to litmus and the pole should be prepared by boiling and cooling, as above directed.

Finally, I wish to point out why earlier determinations resulted in different values for the electromotive force of nickel. Neumann (1) prepared his nickel pole by electrolysis; hence his nickel contained hydrogen and gave too high a potential. Siemens (2) resorted to alternate cathodic and anodic polarization, and finally prepared some nickel by electrolytic deposition, with special precautions as to possible contamination from anodic products. But none of his directions are of any essential benefit—in fact, anodic and cathodic polarization are objectionable. Euler (3) directs that samples of nickel be kept in nickel sulphate solution from 6 to 8 days, and he advises the expulsion and exclusion of the air from the electrolyte, but he does not urge the latter, and he says nothing special about acidity. He obtained with three different samples of nickel the value Ni–N/1 $NiSO_4$ = 0.466 volt. This accords with my own results when the slight differences in procedure are allowed for.

The Effect of Occluded Hydrogen.

Raoult (14) found that a piece of very porous nickel, after polarization in water, evolved 165 volumes of hydrogen when allowed to remain in water for two or three days afterward. He found that there is considerable difference in the amount of hydrogen occluded by different samples of nickel, less porous samples occluding very little. Thoma and others (16) also observed that nickel, on polarization, absorbs hydrogen. It is commonly considered that the "curling up" of electrolytically deposited nickel plate is due to the codeposited hydrogen (17). If the nickel has been deposited very rapidly a

greater amount of hydrogen is enclosed; the uneven escape of this produces a strain in the plate and the latter cracks and peels off. Any agencies which lessen the amount of enclosed hydrogen (such as small current densities or higher temperature)(18) tend to prevent this trouble.[1]

None of these experimenters have studied the effect of hydrogen upon the potential of nickel. Hence my first effort was directed to ascertain this. I took good commercial sheet nickel which had been lying exposed to the air, and placed it in a wide test tube in such a way that a narrow strip or "lip" of sheet nickel extended through a slit in the rubber stopper which closed the test tube. Two glass tubes also passed through the stopper: one, which extended just through the stopper, was bent in the shape of a syphon; the other tube extended to the bottom of the test tube. The test tube was filled with N/1 nickel sulphate solution and closed with the rubber stopper, so that all the air was excluded. By means of the liquid in the syphon tube and of the "lip" of sheet nickel, electrical contact was made. The potential of the nickel at first was 0.30 volt. It rose steadily until after three days it was 0.470 volt, and remained there for two days. Hydrogen gas, prepared by electrolysis with nickel poles in sodium hydroxide solution and filtered through a cotton plug, was now passed through the solution by means of the tube which reached to the bottom of the test tube. The potential rose to 0.62 volt almost immediately. The test tube and contents were now heated to boiling to expel the hydrogen as much as possible. The apparatus was so arranged that on cooling nothing but boiled nickel sulphate solution was drawn into the test tube. At ordinary temperatures the nickel then showed a potential of 0.50 volt. Very little change in this potential was observed during two days. Then the apparatus was completely shut off from contact with air by dipping the end of the syphon tube into mercury, and thus it was allowed to stand for three weeks. After this time the potential of the nickel was 0.48 volt. On

[1] The results of Baxter (20), Sieverts (26), and others on the absorption of hydrogen by nickel at high temperatures have probably no direct connection with the results obtainable at ordinary temperatures.

repeating the experiment I obtained the same results, except that the hydrogen caused a rise of potential to 0.605 volt only.

It is evident that occluded hydrogen raises the potential of solid nickel. The next question of interest is: What is the potential of finely divided *porous* nickel (reduced by hydrogen at a low temperature), and has hydrogen the same effect upon it? The question, as applied to iron, has been answered with great care by Richards and Behr (10), and hence the results for nickel become doubly important, because, through comparison, a check can be made on the potential of nickel.

Pure nickel nitrate (Kahlbaum's)—free from cobalt—was subjected to two fractional crystallizations, and was then dried and ignited in a platinum dish. The resulting nickel oxide was reduced by a current of hydrogen in an ordinary combustion furnace. The hydrogen was prepared from zinc and sulphuric acid and conducted through acidified potassium permanganate solution, then over dry sodium hydroxide, and finally filtered through a bit of cotton. The sample of nickel thus reduced was allowed to cool in hydrogen and was then transferred to a little cup made as follows: Into the bottom of the "cup" of a "thistle top" funnel was fused a piece of platinum wire in such a way that a short portion of it extended into the cup and the other into the stem below, which was completely closed by fusion just below the cup, and was bent up until it touched the cup. The nickel was well tapped into this cup so that none of the platinum wire was exposed. The stem of the funnel was passed through one hole of a rubber stopper which fitted into a 500 cc. flask. Through the stopper also passed two other glass tubes, one of which extended to the bottom of the flask and the other ended just below the stopper. By means of these two tubes a current of gas or liquid could be introduced into the flask. The flask was filled with hydrogen gas and then N/1 nickel sulphate solution, which had been previously boiled and cooled in an atmosphere of hydrogen, was admitted. Electrical connection with the nickel was made by

means of mercury poured into the stem of the cup, and the calomel electrode was connected through the liquid in one of the glass connecting tubes. Under these conditions the nickel showed the following potentials:

At first, volt.	After 12 hrs., volt.	After 24 hrs., volt	After 36 hrs., volt.
0.56	0.59	0.60	0.59

The flask and contents were now heated until the liquid boiled and all hydrogen gas was expelled. The conducting tubes on the outside were connected with the second flask in which nickel sulphate solution was boiled so that when the steam in the closed flask condensed, the solution from the second flask was drawn over, completely filling the first flask. After the flask and contents had cooled thoroughly, the nickel showed a potential of 0.535 volt, which it held steadily for 24 hours. The second sample of nickel was prepared just in the same way as the first, but after the reduction was complete the hydrogen was displaced by a current of pure nitrogen obtained from air by treatment with a large excess of alkaline pyrogallate solution. The flames were then turned out and the nickel allowed to cool in this atmosphere. This nickel was introduced into the cup as above, and the flask filled with nitrogen gas. This was displaced by nickel sulphate solution which had been boiled and then cooled in an atmosphere of nitrogen. This nickel gave a potential of 0.522 volt, which it maintained for 24 hours. After two months its potential was 0.518 volt, while a piece of commercial sheet nickel in the same apparatus with it showed 0.487 volt. It appears from this that the potential of finely divided porous nickel is about 0.52 volt, or about 0.04 volt greater than the potential of solid nickel. Richards and Behr found the potential of porous iron to be 0.03 volt greater than that of solid iron (0.71 volt). The nickel that has been cooled in hydrogen shows a considerably (0.07 volt) greater potential. Heating the nickel in the boiling electrolyte evidently removed most of the hydrogen, but a small amount remained and was removed only by slow diffusion. In this respect the spongy nickel behaved like solid nickel. Richards and Behr also

found it very difficult to remove the last traces of hydrogen from iron.

I proceeded next to ascertain the effect of hydrogen produced in the nickel by cathodic polarization.

A nickel cathode polarized in an acid may show, while polarized, any potential from 0.50 volt upward to 1.00 volt and over. When the current is cut off, the polarization potential sinks more or less rapidly until it arrives in the neighborhood of 0.50, where it appears to stop. With samples of nickel which do not appear to be porous the drop takes place very rapidly, while with porous samples, several days may be required.[1] The maximum of polarization can be observed only while the polarizing current is turned on. Of course, this measurement can be made only by some means which will avoid the introduction of the drop in voltage due to resistance within the electrolyte. This object is usually attained by connecting the calomel electrode through a tube drawn to a fine capillary, the end of which is bent so that the opening may be applied right against the electrode. Mechanical means for disconnecting the electrolyzing current and quickly connecting the auxiliary electrode do not give the maximum polarization values, but give an irregularly lower value. As is well known, these are all characteristics of hydrogen polarization on such metals as platinum, gold, mercury, etc.

When the polarized cathodes are quickly transferred to N/1 nickel sulphate solution they show a higher potential than they showed just before being transferred and while they were in the acid. This is what we would expect, for the concentration of the hydrogen ions in the neutral nickel sulphate solution is much smaller than in the acid. Such trials can be made only when the poles have arrived at the point where the drop in potential is very slow, and even then they can be made successfully only with samples with which the drop in potential is altogether slow—that is, with samples

[1] A porous surface may be readily obtained by means of electrolytic deposition with a relatively large current, alternating short periods of deposition with longer periods of rest.

which are comparatively porous, or in which the occluded hydrogen has penetrated to a considerable depth. Muthmann and Fraunberger prepared such a sample by long polarization in pure water. By this means, these experimenters obtained 0.88 volt as the maximum value. The highest value I obtained by this method is 0.84 volt. But I attach no special significance to obtaining any particular one of these values because it seems to me to be only a question of how rapidly the metal is transferred, how porous it is, etc. (see page 230).

When nickel has been allowed to remain in hydrochloric or dilute sulphuric acid for some time it will show a potential of about 0.40 volt. If it is then well rinsed with distilled water and dipped into N/1 nickel sulphate solution, it will show a potential of 0.50 to 0.65 volt and more. However, if the solution is then made faintly acid, the potential will fall, and with stronger acidification, the potential shown will be 0.45 or even 0.40 volt. This effect of acidification was also observed by Muthmann and Fraunberger. It is readily understood when we recall that nickel can displace hydrogen from acids. Although the hydrogen in the deeper recesses may be very concentrated as a result of the action of the capillary forces, that of the outer layers, which shuts out the electrolyte from the deeper recesses, cannot be concentrated beyond the point at which its solution tension is equal to that of the nickel, and since this "surface" hydrogen is constantly suffering a loss through diffusion the potential exhibited will be *less* than that of the nickel.[1] The drop in potential observed when a nickel sulphate solution is acidified is the result of the same conditions just described. On account of this observation, Muthmann and Fraunberger ascribed to

[1] It might be objected that the potential of nickel in contact with an electrolyte containing none of its ions should be greater than that which it shows when in contact with N/1 nickel sulphate solution. However, it is a matter of common experience with other metals, copper, zinc, etc., that no such great difference exists, and the explanation is that the layer of liquid on the surface of the metal is almost immediately changed to a solution of a salt of the metal. Still it may be objected that if the potential due to the nickel is greater than that due to the hydrogen, the potential due to the nickel should be the one observed. This would be the case if nickel did not possess an extremely small velocity of solution. The loss of hydrogen by diffusion probably takes place comparatively rapidly and the nickel keeps up the supply by reaction; this, together with a small solution velocity, prevents the nickel from exerting its maximum solution pressure.

sulphuric acid a passivizing influence, but in the light of the facts to be presented later, acids are shown to be *activizing* and not passivizing agents. The discrepancy in the interpretation is due to the difference in the location of the equilibrium potential of nickel.

The following procedure enabled me to get the greatest occlusion of hydrogen and hence the highest potential. A piece of sheet nickel was boiled in concentrated sodium hydroxide solution for 15–30 minutes,[1] and then placed in concentrated hydrochloric acid for the same length of time. It was then rinsed with water and placed in N/1 nickel sulphate solution which had been boiled (to remove the air) and cooled. This sample showed a potential of 0.875 volt for five days afterwards. A striking behavior of this electrode showed itself when it was again used as a cathode. Before the current was turned on it showed the high value just above mentioned, but as soon as a current of very low density was turned on, the potential dropped to about 0.50, rising from this on with the current density. A day or two after the current was cut off, the electrode exhibited the former high potential. This behavior is characteristic of polarization phenomena and was first observed by Helmholtz (8) and by Fromme (19). It is considered to be due to the fact that the gas which is deepest down in the pores diffuses out very slowly, and is at a greater concentration, corresponding to the greater potential exhibited. When the current is turned on, the gas in the surface separates the electrolyte from the gas farther down in the pores, and the potential shown is that of the surface gas. When this has escaped the electrolyte penetrates to the more concentrated gas, and the potential of the latter shows itself again.

These results show that occluded hydrogen may raise the potential of nickel considerably above 0.48 volt.

Since, in the deposition of nickel, hydrogen is always co-deposited, the effect of this hydrogen upon the deposition potential of nickel will be considered next.

[1] This probably forms a sodium-nickel alloy, the subsequent decomposition of which leaves the nickel in a very porous condition.

The first determination of the least cathode potentials with which nickel is deposited was made by Kuester (6). He found nickel to be deposited out of neutral N/1 nickel sulphate solution at 0.80 volt. With acidified, or with more dilute, solutions a higher potential is required. Coffetti and Foerster (7) found that nickel was deposited out of N/1 nickel sulphate solution acidified with N/400 sulphuric acid under the following conditions: current density, 0.113 ampere per 100 sq. cm.; cathode potential, 0.903 volt; current yield, 20 per cent. One may infer from their article that they were unable to deposit nickel at a lesser potential.[1] I found that nickel may be deposited out of neutral N/1 nickel sulphate solution on a sheet nickel cathode at considerably lower potentials. The results attained with the lowest potentials employed are as follows:

(*a*) Perfectly neutral N/1 nickel sulphate solution was employed in the apparatus described at length in the first part of the following paper on "The Behavior of the Nickel Anode." The large pole was used for the cathode, and the anode was placed inside of the porous tube. The current density at the cathode was 0.026 ampere per 100 sq. cm., and the cathode potential, 0.75 to 0.76 volt. The amount of deposit obtained is 0.1265 gram, which represents 55 per cent of the current used. In a second trial under the same conditions, 0.110 gram were deposited, representing 45 per cent of the current used.

(*b*) Since the potential of nickel in N/1 nickel chloride is approximately the same as in N/1 nickel sulphate solution, the deposition potential for nickel chloride solution should not be essentially different from that for sulphate solutions. The apparatus employed for these determinations (which is the same as that employed for the depositions at higher temperatures described below) was unintentionally different from that employed above. A current density of 0.05 ampere

[1] Coffetti and Foerster (7) state that Kuester (6) found the least deposition potential of nickel out of N/1 nickel sulphate solution to be 0.90 volt, and they argue that this value gives a remarkable support to Muthmann and Fraunberger's value, 0.88 volt. If their reference is correct, then their quotation is erroneous and the argument has no basis.

per 100 sq. cm. gave a cathode potential of 0.675 volt. The amount of the deposit obtained was 0.022 gram, which represents 23 per cent of the current used. In a second experiment the potential was 0.69 volt and the current yield 26 per cent.

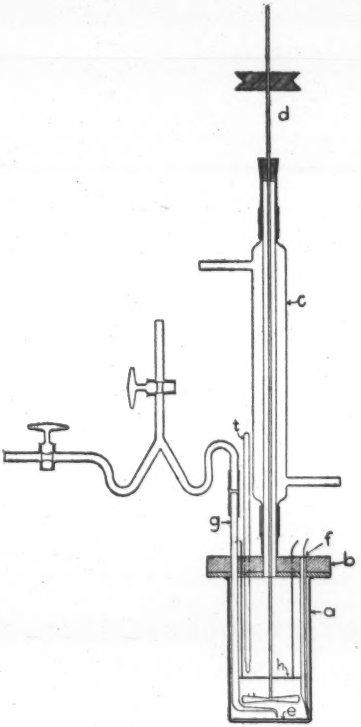


Fig. 1.

The deposits obtained in the preceding experiments were all of dull appearance, and hence were open to the suspicion of being deposits of basic salts rather than of the metal. However, such films would have introduced surface resistances and would have influenced the potential. Since no such influences were observed we may conclude that the deposits were essentially of pure metal.

At best these results leave a wide gap between the equilibrium potential, 0.48 volt, and the least deposition potential observed with sulphate solutions, 0.75 volt. This appears to be an objection to the acceptance of 0.48 volt as the correct value for the equilibrium potential. However, the following deposition experiments at higher temperatures will help to remove this objection.

Figure I. shows the apparatus employed in these determinations. *a* is a thin porcelain beaker, 8 x 20 cm.; *b*, a well-fitting cover of soft sheet rubber reinforced with a piece of hard rubber; *c*, a small condenser; *d*, a long glass rod, to the lower end of which two glass turbine vanes are attached and which is fitted near its upper end with a pulley; *e*, a circular sheet nickel electrode with a long narrow strip, *f*, extending through a glass tube which insulates it from the solution; *g*, tube providing connection with the calomel electrode—the lower end is drawn out to a fine capillary; *h*, the upper circular sheet nickel electrode—held in place by two narrow strips of nickel; *t*, a thermometer. The tube *g* was left sufficiently loose in the cover so that potentials at different points of the lower electrode might be observed. The curves in the tube connecting with the calomel electrode prevented a mixing of the liquids by convection currents. The lower electrode was used for the cathode. Before weighing it, it was washed first with water, then with alcohol, and dried by gentle warming. The beaker and contents were heated in a large water bath. The results obtained are given in the following table:

Number.	Solution.	Temperature.	Ampere per 100 sq. cm.	Amount of deposit in grams.	Yield in per cent of current.	Cathode potential.	Remarks.
1	N/1 $NiSO_4$	98°	0.25	0.2083	90	0.59–0.63	Plate bright
2	"	98°	0.25	0.2310	88	0.59–0.63	"
3	"	98°	0.05	0.0375	90	0.53–0.59	"
4	"	98°	0.05	0.0403	91	0.53–0.59	"
5	"	80°	0.05	0.0192	65	0.73	Deposit dull
6	"	80°	0.05	0.0401	68	0.74	"
7	N/1 $NiCl_2$	98°	0.05	0.0598	78	0.51–0.53	"
8	"	98°	0.05	0.0461	75	0.51–0.53	"

In Nos. 1 to 4 the cathode potential fell rapidly to 0.47 volt when the circuit was opened. The equilibrium potential at 98° is between 0.42 and 0.44 volt.

The results with N/1 nickel chloride solution are added merely to indicate that there is nothing peculiar in the behavior of nickel sulphate as contrasted with other salts. Since the nickel chloride is hydrolyzed when cold the solution was filtered (cold) before it was used.

The lowest deposition potential with N/1 nickel sulphate solution shown above is still at least 0.09 volt above the corresponding equilibrium potential, but it is much nearer the latter than is the case at ordinary temperatures. And since at 98°, even with as small a current density as 0.05 ampere, nickel is deposited in the main (90 per cent), the deposition of nickel takes place even with lesser current densities and cathode potentials. The general relation of the cathodic polarization to the current density at 98° is here given.

N/1 Nickel Sulphate at 98°.

Current density in amps. per 100 sq. cm.	Cathodic polarization.	Current density in amps. per 100 sq. cm.	Cathodic polarization.
0.004	0.50	0.075	0.60
0.008	0.525	0.150	0.61
0.015	0.555	0.375	0.625
0.040	0.565	0.750	0.65

The curve plotted from these figures is given in Fig. II., in which are shown, for comparison, the curves for the deposition

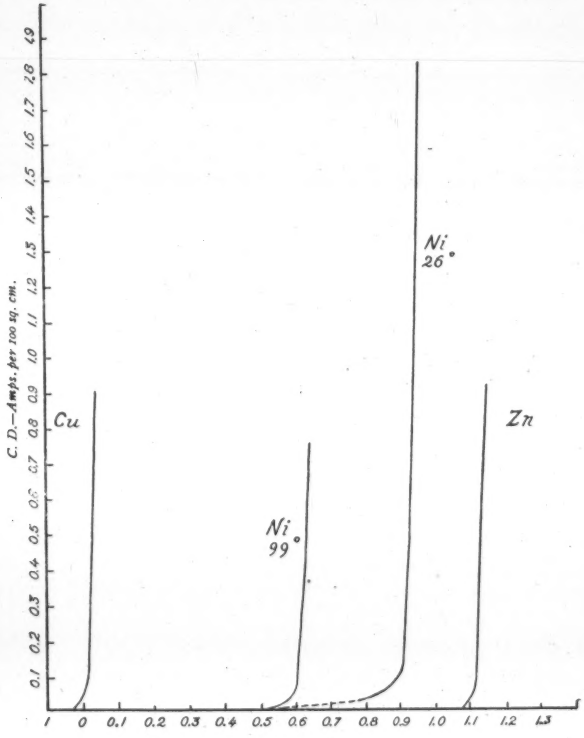


Fig. II.—Cathodic polarization values.

of copper out of N/1 copper sulphate, zinc out of N/1 zinc sulphate, and nickel out of N/1 nickel sulphate solution,[1] all

[1] Most of the data for the last three curves are from Coffetti and Foerster's paper (7).

three at ordinary temperatures. It is seen that the main portions of all the curves, with current densities above 0.1 ampere, are almost parallel. They are nearly straight lines—possibly logarithmic curves, as they should be in accordance with Nernst's formula. This part of the curve for nickel sulphate at 25° had given much support to the idea that the equilibrium potential of nickel might be 0.88 volt because when this curve is continued similarly to the curve for copper and zinc the point corresponding to 0.0 current would be 0.88. In the same way the upper part of the curve for nickel at 99° would lead to another potential, about 0.55 volt. Thus it appears as though the deposit obtained from nickel solutions with larger current densities is a metal with a *particular potential*, which varies with temperature. However, with small current densities the curves turn suddenly so that the continuation makes a very small angle with the "potential" axis. The data for some well-established points on these portions of both curves are given by my experiments above. The continuation of this portion of the curve for 99° shows that the point corresponding to 0.0 current is approximately at 0.44 volt, and thus indicates that the equilibrium potential of Ni-N/1 nickel sulphate solution at 99° C. is correctly located.

It follows that at ordinary temperatures either the equilibrium potential is much higher, or some special cause operates to prevent the deposition of nickel except with cathodic potentials 0.2 to 0.3 volt above 0.48 volt. Such an influence of temperature upon the equilibrium potential would be unique and surprising and as the behavior of the nickel pole in all other respects points to 0.48 volt as the equilibrium potential, we will dismiss the first possibility stated above and endeavor to point out the "cause" of the "gap" between 0.48 volt and the least deposition potential.

In the literature on the subject of deposition potentials is found the idea that the phenomenon is due to a "deposition resistance," an idea advanced by Kuester (6 and 21) in connection with the deposition of iron-nickel alloys. He and Toepfer (22) found that with very small current densities a

trace of nickel alone may be deposited out of the solution containing both iron and nickel, but with greater current densities iron is codeposited in a greater proportion than its proportion to nickel in the solutions. Since the deposition potential of iron out of a separate solution under the same conditions is at least 0.1 volt higher than the deposition potential of nickel, this preponderance of iron over nickel in the deposit is very surprising. Kuester reached the conclusion that the resistance to the deposition of iron is greater than that to the deposition of nickel. But the proof he advances, which involves the use of nickel and zinc, is not convincing, for these two metals differ considerably in their excess tensions and this was not taken into account by Kuester.

Foerster (11) has recently set forth again the idea of *deposition resistance*. He shows that at higher temperatures the "cathode potential"-"current density" curves of *cyanide* and of *ammoniacal* solutions of copper, zinc, silver, and cadmium salts diverge less from the "current density" axis than they do at lower temperatures, and he argues that this influence of temperature indicates that we have to deal with a chemical or "reaction resistance." The application of this idea of deposition resistance to the deposition of nickel is also being considered by Foerster, but in this he has reached no decision so far.

Though this idea of "resistance" has much to command it, I am of the opinion that the cause of the "gap" is found in special *potential* relations which exist between the deposit and the solution. The possibility of such novel relations first revealed itself in connection with a study of the deposition of nickel-zinc alloys, which I carried out in conjunction with Mr. A. Hirsch (23 and 24).

The same surprising relations between the composition of the solutions and the alloy deposited therefrom which is shown by nickel and iron is shown much more strikingly by nickel and zinc. The ratio Zn: Ni in the alloy is from 4.3 to 24 times the ratio Zn: Ni in the electrolyte. This preponderance of the deposition of zinc over that of nickel cannot be due es-

sentially to a difference in "reaction velocity," for the following reasons: With very small current densities nickel should be deposited free from, or with very little, zinc, because the deposition potentials of the two metals singly are 0.25 to 0.30 volt apart; but deposits obtained with the least possible current density contained never less than 30 per cent zinc and usually nearly 80 per cent. A striking example is here given in detail (24): Current density, 0.1 ampere per 100 sq. cm.; current yield, 26 per cent; amount of deposit, 0.0326 gram; ratio (*a*), *Zn*: *Ni in alloy*, 4: 1; ratio (*b*), *Zn*: *Ni in electrolyte*, 1: 6; ratio *a*: *b*, 24: 1.

An insight into the underlying causes that produce these results was obtained through the following two experiments:

(1) *The Determination of Least Cathodic Deposition Potential upon a Mercury Cathode.*—The mercury cathode prevented the evolution of hydrogen. Of course, nothing is known concerning the composition of the deposits formed under these conditions, and the potentials observed are all somewhat irregularly lower than those which would have been observed on other poles (*e. g.*, platinum), yet it may be claimed that the picture of results obtained shows points which must have corresponding points in the normal state of affairs. The curve of the results is shown in Fig. III.

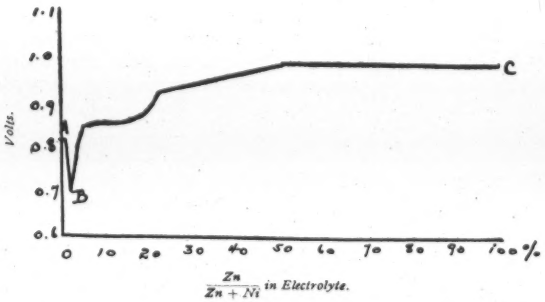


Fig. III.—Least cathode potential for deposition of nickel-zinc alloys.

A surprising state of affairs revealed itself: Nickel, when present alone, shows one particular least deposition potential, but when zinc is present in any amount above 7 per cent (approximately), then no current flows—nothing is deposited—until a higher potential, varying with the composition of the solution, is reached. This shows that a metal in the presence of a second metal may not be deposited on a cathode which is at a higher potential than that at which the metal, if present by itself, would be deposited. This is not due to a resistance, because as soon as the deposition potential of the solution is exceeded, the deposition takes place without any noticeable hindrance. It is probable that deposition can take place only when the potential of the resulting alloy is exceeded by the cathode potential.[1]

(2) *The Determination of the Relation of Zinc to Nickel in the Solution which is in Equilibrium with Any Particular Sample of "Nickeled" Zinc Dust.*—With one such sample equilibrium was attained when the solution contained 2.2 per cent of nickel by equivalents. The total concentrations of the solution ranged from two normal to half normal, and at the beginning some of the solutions contained less and others more than this proportion of nickel. From the Nernst formula for the potential of a pole, it follows that these metals in the alloy must have very nearly the same solution tension. Since the alloy consists mainly of zinc with only a small amount of nickel, it follows that the solution tension of nickel in this alloy is much greater than that of pure nickel. Thus it appears that a metal, when alloyed, may have its potential raised. Naturally, it will then require a higher deposition potential.

Of the two ideas set forth in the preceding pages, that of a *special potential* relation accords better with the facts observed

[1] The composition of the alloy is determined by the mutual solubility—or alloying tendency—of the two metals, and this is probably the fundamental cause of the deposition of the large percentage of zinc. This view accords with well-established principles: For instance, in Fig. III. the portion of the curve A to B corresponds to the formation of nickel with gradually increasing amounts of zinc dissolved in it, and hence to falling potentials; the portion C to B corresponds to the formation of zinc with gradually increasing amounts of nickel dissolved in it, and hence also falling potentials. The two curves cross in B.

in the deposition of nickel than the idea of a *reaction resistance*. This becomes evident when the curves for the deposition of nickel and other metals (see page 225) are recalled. It was pointed out in connection with the curves for nickel that the portions with current densities above 0.1 ampere per 100 sq. cm. are of such a form as to indicate that the deposit obtained at any one temperature is a metal with a definite potential, which is less at higher temperatures. Since hydrogen is codeposited with nickel, and the deposits exhibit potentials above that of nickel, it is quite likely that, with large current densities, the deposited metal takes up the maximum amount of hydrogen which it can hold at that temperature and hence the deposit exhibits a maximum potential (0.88 volt at ordinary temperatures; 0.55 volt at 99°). Schoch and Hirsch found (23) a similar relation in the deposition of zinc-nickel alloys; with increasing current densities, the composition of the alloys obtained finally becomes constant with a maximum per cent of zinc. With current densities less than 0.1 ampere, the nickel-hydrogen particles separated from the solution contain (probably) less hydrogen than the maximum amount and hence they may be deposited at lower potentials. The lowest limit of potentials that can be thus obtained is probably fixed by the composition of the solution—just as was found to be the case with the nickel-zinc solutions—and hence this lower limit may be considerably above the equilibrium potential of nickel—in a sense it has no direct connection with it.

Thus we see that the idea of potential relations similar to those found with nickel-zinc alloys fits every known detail concerning the deposition of nickel.

Though there may be many possible explanations involving the idea of a reaction resistance, yet it seems to me that none will be able to overcome the fundamental difficulty, namely, that with potentials below 0.88 volt the resistance would have to be very great, while with potentials above 0.88 volt it would be zero or very small. Such a *sudden* change is incompatible with the idea of a *resistance* influence.

This "proof" of a special potential relation is probably in-

complete. Whether the "gap" is due to a *resistance* or to a *potential* phenomenon is still an open question, but that the existence of the "gap" should be an argument against accepting 0.48 volt as the equilibrium potential of nickel has, I think, been rendered unlikely.

Summary.

1. The potential of nickel in N/1 nickel sulphate solution is 0.48 volt.

2. This is the true reversible potential, because it is attained from both sides as the final point of equilibrium.

3. Occluded hydrogen raises the potential of nickel. The deposition of the metal does not take place except at potentials 0.2 to 0.3 volt above 0.48 volt because hydrogen is codeposited and, in general, deposition cannot take place until the potential of the particles to be deposited is reached.

In conclusion, I wish to express my appreciation of the help which Mr. H. S. Bonham, of this laboratory, has given me in some of the experimental work.

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[Contributions from the Chemical Laboratory of the University of Texas.]

THE BEHAVIOR OF THE NICKEL ANODE AND THE PHENOMENA OF PASSIVITY.[1]

BY E. P. SCHOCH.

A number of investigators have studied the behavior of the nickel anode in connection with "passivity." But no one has studied it with the view of locating the equilibrium potential, and no one appears to have started his observations from any particular potential.

Hittorf (4) studied nickel briefly in connection with his general investigation of passivity. His work is, in a sense, mainly qualitative, and since his results are now found in textbooks, it is unnecessary to repeat them here.

Le Blanc and Levi (5) determined the extent of action of different electrolytes upon nickel anodes. They noted also the effect of temperature. The effect of current density was not studied in detail, and the anode potential was observed only approximately by noting the voltage drop between the poles. They found that hydrogen and halide ions increase the anodic solution of nickel markedly, also, that increase of temperature increases the action of electrolytes on the nickel anode.

Foerster and Piguet (1) determined the anodic potential

[1] See footnotes 1–3, p. 208 of preceding paper on "The Electromotive Force of Nickel."

with which oxygen is evolved from 2 N potassium hydroxide solution on a nickel anode in comparison with anodes of platinum and iron. They found that oxygen is evolved on nickel at a lower potential than on iron (difference, 0.12 volt) and at much lower potential than on smooth platinum (difference, 0.32 volt). They also noted in this connection that no determinable quantity of nickel is dissolved, and the surface remains perfectly bright—no oxide is formed.

E. Mueller and Spitzer (2) determined the conditions under which nickel oxide is precipitated out of a solution upon a platinum anode, and then determined the potentials at which oxygen is evolved on platinum, nickel, and nickel oxide deposited on platinum. They had found that with cobalt and iron, respectively, oxygen is evolved on the metal at the same potential as on the oxide, and at a much lower potential than upon platinum. With nickel, however, the following figures were obtained:

	Volts.
Platinum	1.416
Nickel	0.900
Nickel oxide	0.540

Hence, the same statement cannot be made for nickel as for cobalt and iron.

Fredenhagen (6) determined the "current-density: anode-potential" curves of nickel in N/10 and N/1 sulphuric acid and N/1 hydrochloric acid, as obtained with *increasing* and *decreasing applied electromotive forces*, respectively. With sulphuric acid, he finds a sharp turn in the curves with increasing applied electromotive forces, which indicates that the anode has suddenly become almost insoluble. In the curve obtained with decreasing applied electromotive forces the "turn" occurs at another point. With N/1 hydrochloric acid and with sulphuric acid at high temperatures there is no such critical turn in the curves, and they bend away much less from the current density axis than the curves for sulphuric acid at ordinary temperatures.

Sackur and Alvares (7) studied the behavior of the nickel anode in the same manner as Fredenhagen. They worked

with from 5 N to 0.15 N sulphuric acid and found an approximate proportionality between the concentration of the hydrogen ions and the "critical current density" which just precedes the "turn" to passivity. Then they tried the effect of the addition of halide ions and found it also proportional to their concentration. Finally they found that passive nickel is still slightly soluble.

The purpose of my own experiments was to start with the nickel anode under equilibrium conditions—*i. e.*, in neutral nickel sulphate solution, and at the equilibrium potential—and to study its behavior as these conditions are gradually departed from.

In designing the apparatus the following points had to be considered:

(*a*) To remove and exclude oxygen, and to prepare the pole—*i. e.*, the surface of the metal—in as definitely reproducible a manner as possible.

(*b*) To stir the liquid next to the anode surface so effectively that any further increase in the rate of stirring produces no noticeable effect. This, with a relatively large volume of solution, insures constant composition of the solution next to the anode.

(*c*) To use a large anode surface because many of the current densities employed must be very small, and with a small anode surface, irregular influences may easily distort the results.

(*d*) Since many of the current densities to be employed are of the dimensions of "rest-currents"—*i. e.*, currents depending upon the convection of hydrogen to the anode—and since the potential of nickel may be influenced by hydrogen, the introduction of hydrogen into the electrolyte had to be absolutely prevented.

The apparatus designed with these points in view is shown in Fig. I. *a* is a large test tube, 5 x 25 cm.; *b*, a cylinder of sheet nickel which fits closely into the test tube (area of inner surface, 270 sq. cm.); *c*, a rubber stopper; *d*, a porous earthenware tube, 2 x 25 cm. (Pukall filter tube), open at both ends; *e*, a rubber stopper closing *d*; *f*, a glass tube; *g*, a stirrer of glass

rod (this fits closely into the glass tube *f*); *h*, a short piece of rubber tubing; *i*, a pulley; *k*, a glass tube with one end drawn to a capillary, which serves to connect the calomel electrode (the two liquids meet at the Y joint, and the curves prevent the convection currents from mixing the liquids); *l*, a thermometer (not shown—it is inserted through *c*); *m*, a thin lead

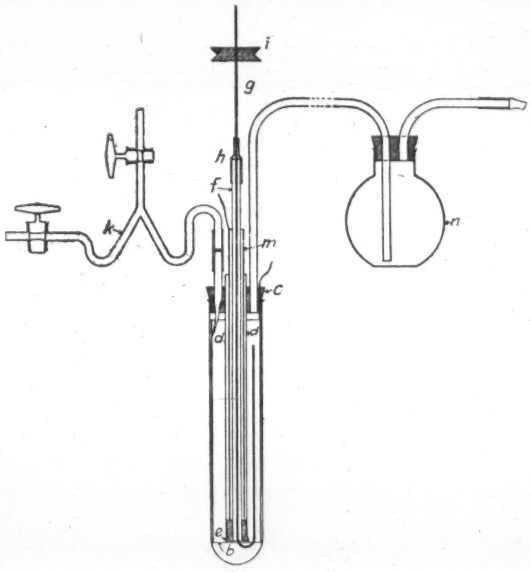

Fig. I.

pipe whose surface has been converted into lead peroxide (this serves as the cathode and eliminates the evolution of hydrogen); *n*, a flask which holds the excess of electrolyte (the level of the liquid in it is above the top of the test tube so that in the event of a leak anywhere air would not be admitted but liquid would be forced out through the leak).

In an operation, the test tube is nearly completely filled with the electrolyte, and a sufficient excess is poured into the flask with which the syphon connects. After the apparatus is properly closed and connected up, the liquids are boiled vigorously for several minutes, until with a slight lowering of the temperature and the condensing of the steam the test tube and syphon fill completely with the electrolyte. The stirrer is turned at a rate of about 200 revolutions per minute. With this apparatus and procedure the following results were obtained:

Electrolysis of N/1 Nickel Sulphate Solution, at 25°.—Table of Characteristic Polarization Values (See *b* below).—*Curve I.*

Current density[1].	Potential[2].	Current density.	Potential.
0	0.475	12	0.27
0.04	0.47	16	0.222
0.08	0.463	24	0.123
0.12	0.457	32	0.05
0.2	0.445	36*[3]	.....
0.4	0.432	..	.....
0.8	0.42	14	—0.885†[4]
2.0	0.39	24	—1.06 †
4.0	0.36	185	—1.131 †
8.0	0.315	..	.....

Special observations on the electrolysis with neutral N/1 nickel sulphate solution:

(*a*) The potentials obtained with current densities less than 4 milliamperes are readily reproducible; *i. e.*, approximately the same potentials are obtained with increasing or decreasing current densities as long as the limit 4 milliamperes has not been reached. This behavior is commonly considered to be *normal* anodic behavior.

(*b*) Beyond this limit the results are no longer reproducible; if the current density applied is not excessive, then the po-

[1] All current densities are expressed in *milliamperes* per 100 sq. cm.

[2] All potentials spoken of in this paper are *anode* potentials, unless it is specially stated to be otherwise.

[3] In this and the following tables the current density with which passivizing sets in immediately is marked by an asterisk (*).

[4] The potentials shown by the anode in the passive state will be marked thus (†).

tential of the pole may become stationary within a few minutes and may remain so for a long period (30 to 50 minutes and even longer). With excessive current densities the potential will continue to drop indefinitely—until the evolution of oxygen sets in. However, the stationary potential obtained with the same current density has different values depending upon the previous treatment: *e. g.*, the amount of preceding

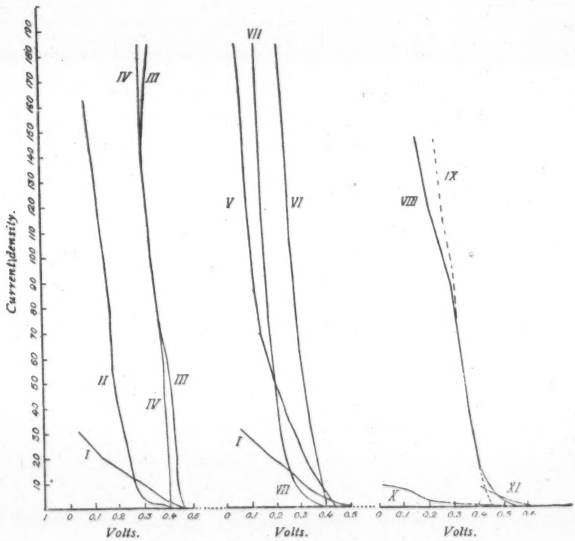

Fig. II.—Nickel anode-polarization values.

electrolytic action, the periods of rest, etc. In short, the values are not reproducible. Thus with a current density = 7.4 the following two stationary conditions were maintained for one hour: one at 0.32 volt, and the other at 0.024 volt. If to a newly prepared pole a particular current density is applied until a stationary condition is reached, the two sta-

tionary conditions are often not attained in the same time, and the final potentials are not the same. Thus, with a current density = 11, the stationary potential attained in one case was at 0.123 volt and in another at 0.012 volt. These stationary potentials appear to be determined by the accidental conditions of the pole surface which result from the electrolysis.

This state of affairs requires the framing of an arbitrary rule for selecting the potential values corresponding to the different current densities. I found that satisfactory reproducible results are obtained when the current densities employed form an increasing series of values and the time of operation of any one current density is from ½ to 2 minutes, approximately. All values for the curves in this part have been so obtained.

With this procedure the condition of the anode can be reliably identified—as will develop farther on—and hence these values are designated as characteristic polarization values.

(*c*) The chemical action which takes place as long as the potential for the evolution of oxygen has not been reached is a quantitative solution of the nickel. Thus, for example, in an electrolysis with neutral N/1 nickel sulphate solution in which the potential dropped as low as —0.17 volt for a part of the time (but no lower) the anode lost 0.1100 gram during the whole operation, while the current used required a loss of 0.1058 gram—a fair agreement. Other trials have confirmed this result.[1]

(*d*) There is neither a critical voltage nor a critical current density which terminate the active and mark the beginning of, or change to, the passive state. Thus a current with current density = 24 and an initial potential of 0.123 volt, when allowed to continue for 15 to 20 minutes, produced the condition which we shall call *passivizing*; *i. e.*, even a very small current density produces steadily lower potentials until finally the evolution of oxygen begins. On the other hand, with a current density = 32 and an initial potential of 0.050 volt passivizing did not set in for several minutes. Again with a current density = 7.4 and an initial potential of 0.024 volt, passivizing did not set in even during one hour, which might be considered as showing

[1] See also the results obtained by Byers: J. Am. Chem. Soc., **30**, 1740.

that the pole is in the active state. Yet when the current was raised to current density = 11, passivizing set in immediately. There is evidently no one value which alone marks the beginning of "passivizing." And just as the "stationary" conditions considered under (*b*) depend upon the previous treatment of the electrode, so the conditions for passivizing depend upon the previous treatment.

Furthermore, the change of potential preceding and during "passivizing" may be made to progress as slowly or as rapidly as desired by regulating the current density. Apparently no sudden change is wrought in the anode when "passivizing" sets in.

Fredenhagen (6), Le Blanc (5), and Sackur (7) observed, when using dilute sulphuric acid as the electrolyte, that the change, in voltage, from active to passive state takes place *suddenly*, and Sackur even speaks of a particular critical current density. Hence I consider it important to point out that with nickel sulphate no such state of affairs exists.

(*e*) Whenever the current is discontinued the potential of the pole begins to rise immediately. In general, the rate with which it rises is less as the extent of the preceding electrolysis was greater, and the accompanying potentials were lower. If electrolysis has lowered the potential no further than 0 volt (approximately) then the potential will rise rapidly to very nearly the former maximum value. If electrolysis has been more extensive, and has produced lower potentials, there will be a noticeable pause in the neighborhood of 0.3 volt as the potential ascends. It should be noted that this coincides with the so-called "air" potential.

Even after the pole has regained the equilibrium potential, the surface of the pole has not returned to its former state, as is shown by the fact that at the same potentials, the current densities now supported are much smaller than those supported by the newly prepared pole. This same condition obtains all the more if the pole did not regain even the equilibrium potential.

In the course of time, however, the pole regains its former state gradually. The change can be enormously accelerated

by boiling the pole with its liquid, as is done at the beginning of each operation. With neutral N/1 nickel sulphate solution, a maximum of five minutes' boiling restores the former condition of the surface, irrespective of the amount of electrolysis that has preceded. *It is notable that the surface thus prepared gives the same polarization curve not only with the same piece of sheet nickel after it had been subjected to electrolysis, but also with different pieces of nickel.*

However, this rate of "return" of the surface to its "normal" state is much slower if free nickel hydroxide is floating in the liquid. Thus, to a nickel pole with which a series identical with that for Curve I. had been obtained, and which, after reboiling, had just given the same series, enough potassium hydroxide was added in the anode compartment to precipitate one-tenth of the nickel in solution. After reboiling and cooling it gave the following series:

Current density:	0	3.7	7.4	11.1
Potential:	0.436	0.295	0.197	—0.098

It is evident that the surface has not regained its original state.

Electrolysis with N/1 Nickel Chloride Solution, at 25°.—Table of Characteristic Polarization Values.—Curve II.

Current density.	Potential.	Current density.	Potential.
0	0.418	11.1	0.267
0.04	0.401	18.5	0.246
0.08	0.387	37.0	0.208
0.1	0.381	45.0	0.190
0.18	0.373	75.0	0.175
0.37	0.363	90.0	0.155
0.74	0.344	164.0	0.081
1.11	0.336	370.0	—0.049
1.48	0.327	534.0	—0.098
2.22	0.319	904.0	—0.160
2.96	0.307	1274.0	—0.221
3.7	0.298	1808.0	—0.339
7.4	0.276	2590.0	—0.393
....	.....	3700.0	—0.541

Further remarks on electrolysis with N/1 nickel chloride solution:

(*a*) The solution was filtered cold to remove the basic salts which had been formed by hydrolysis.

(*b*) Frequently it is impossible to obtain any potentials above 0.32 volt when the solution is stirred. In that case, current densities less than 2.22 will produce no lowering of the potential, and the potentials observed with larger current densities will be the same as those obtained in the series above. If the pole is allowed to rest, without stirring, it attains the equilibrium potential (0.418) in almost every instance, but frequently the potential will drop to 0.32 volt again as soon as the solution is stirred.

(*c*) It is seen that there is a sharp turn in the curve at current density = 0.4, which indicates a change in the chemical process.

(*d*) Upon opening the circuit the potential returns quickly to the maximum value (0.32), irrespective of the extent of electrolysis. This shows that the behavior of the anode in chloride and sulphate solutions is essentially different at all except the highest potentials. The potentials in N/1 nickel chloride solution are approximately reproducible, and they soon attain, with any one current density, a stationary condition, indicated by the constancy of the potential. Thus, with current density = 50 the potential shown after 20 minutes and maintained for 3½ hours was 0.17 volt.

Electrolyses at Higher Temperatures—96°.

3. N/1 Nickel Sulphate—Curve III.		*4. N/1 Nickel Chloride—Curve IV.*	
Current density.	Potential.	Current density.	Potential.
0	0.442	0	0.405
0.37	0.44	0.37	0.405
0.74	0.44	0.74	0.405
1.0	0.44	3.7	0.405
1.9	0.436	7.4	0.399
2.6	0.436	11.1	0.393
3.7	0.43	18.5	0.393
7.4	0.424	25.9	0.387
18.5	0.418	37.0	0.375
37.0	0.406	55.5	0.369
55.5	0.393	74.0	0.356
74.0	0.363	111.0	0.325
185.0	0.319	185.0	0.303

Further remarks on electrolyses at higher temperatures:

(*a*) Upon opening the circuit, the potential "jumps" back to the value corresponding to zero current, irrespective of the extent of the electrolysis that has taken place.

(*b*) The values above are but *slightly* higher than the values shown during prolonged electrolysis. Thus, with nickel sulphate electrolyzed for three hours with a current density = 50, the potential remained practically steady at 0.39 volt, while with a current density = 125 it showed 0.34 volt during two hours. With nickel chloride electrolyzed with a current density = 50, the potential remained at 0.36 volt during three hours.

Hence the behavior shown by the nickel anode in the solutions above at 95° C. may be said to be *normal*, both with reference to the chemical actions (which consist of the quantitative solution of the metal) and to the electrical behavior, as set forth above.

Electrolyses with Acidified N/1 Nickel Sulphate Solution.

5.—With N/100 Sulphuric Acid—Curve V.		*6. With N/10 Sulphuric Acid—Curve VI.*	
Current density.	Potential.	Current density.	Potential.
0	0.418	0	0.393
3.7	0.393	3.7	0.375
7.4	0.369	7.4	0.366
18.5	0.319	18.5	0.338
25.9	0.270	37.0	0.313
37.0	0.221	55.5	0.289
55.5	0.172	111.0	0.246
74.0	0.123	185.0	0.204
92.5	0.098	296.0	0.166
111.0	0.085	370.0	0.141
129.5	0.070	555.0	0.095
148.0	0.065	740.0	0.046
166.5	0.057	1480.0	0
185.0	0.046	1850.0	—0.073
222.0	0.043	2220.0	—0.123
259.0	0.009	2580.0	—0.246
296.0	0	2960.0*	.....
333.0	0	.....	.....
370.0	—0.020	2960.0	—1.722†
555.0	—0.028		
529.0*	.....		
.....	.....		
629.0	—1.648†		

When the current is interrupted, the potential returns promptly to the value corresponding to zero current. This takes place even after oxygen has been evolved (at the lowest potentials given).

Electrolyses with N/1 Nickel Chloride Solution Acidified with N/10 Hydrochloric Acid.—Curve VII.

Current density	0	3.7	7.4	19.5
Potential	0.393	0.319	0.270	0.233
Current density	37.000	74.000	185.000	
Potential	0.204	0.172	0.123	

This series of values does not differ markedly from the series obtained with the neutral solution.

In order to be able to study the effect of alkaline solutions in the electrolysis with nickel anodes I substituted N/1 potassium sulphate for N/1 nickel sulphate solution and ascertained the difference in effect due to this change.

Electrolyses with N/1 Potassium Sulphate Solution.—Table of Characteristic Polarization Values.—Curve VIII.

Cur. density	0	0.74	1.85	3.7	7.4	18.5
Potential	0.571	0.524	0.492	0.467	0.442	0.393
Cur. density	37.000	74.000	111.000	148.000	185.0*	
Potential	0.369	0.319	0.221	0.155	....	

Notes on electrolysis with N/1 potassium sulphate solution:

(*a*) The passivizing drop is very sudden. Since this *sudden* drop is always observed with electrolytes for which a large current density is required to produce passivity, it is probably due entirely to the large current and hence it is an *unessential* characteristic.

(*b*) The surface is "impaired" by electrolysis with potassium sulphate just as with nickel sulphate—*i. e.*, it will stand less current density than before at the same potentials. After the current is interrupted, the pole regains the higher potentials just as slowly as it did with nickel sulphate. Boiling restores the surface completely.

(*c*) Much greater current densities can be sustained by the anode at any one potential in potassium sulphate than in

nickel sulphate solution. This is due to a peculiar condition of the surface produced by interaction between the metal and the solution. The same surface, after it was thus effected, produced in N/1 nickel sulphate solution the following characteristic polarization values (see Curve IX.—dotted):

Cur. density	0	1.11	2.22	3.7	7.4	18.5
Potential	0.467	0.442	0.439	0.436	0.418	0.393
Cur. density	37.0	74.0	111.0	148.0	185.0*	
Potential	0.356	0.319	0.270	0.231	....	

This shows that the anode sustains larger current densities in nickel sulphate just as well as in potassium sulphate solution, hence the difference is not due to the liquid. The pole was next subjected to electrolysis in nickel sulphate solution with current density = 3.7 and a potential of 0.197 volt for five hours, with the view to removing the affected surface. Then the apparatus was refilled with another portion of N/1 nickel sulphate solution, which was then boiled and cooled; after this the original characteristic polarization values were obtained again, which shows that the effect is superficial.

It is likely that a nickel-potassium alloy is formed by the interaction of nickel and the solution. The existence of such an alloy has been demonstrated by Siemens (8). That such an action occurs is also indicated by the fact that nickel dissolves extensively in potassium sulphate solution.

Electrolyses with N/1 Potassium Sulphate Solution Alkaline with N/10 Potassium Hydroxide.—Table of Characteristic Polarization Values.—Curve X.

Current density.	Potential.	Current density.	Potential.
0	0.565	11.1	—0.369†
0.37	0.430	18.5	—0.418†
0.74	0.282	25.9	—0.442†
1.11	0.240	37.0	—0.454†
1.85	0.196	55.5	—0.467†
2.59	0.180	74.0	—0.473†
3.7	0.166	111.0	—0.492†
5.55	0.135	148.0	—0.51 †
7.4	0.073	185.0	—0.524†
9.25	0.024	370.0	—0.590†
11.1*			

Several minutes elapsed before the potential corresponding to current density = 0.37 became "steady."

The passivizing "drop" which began with current density = 11.1 was very slow. With the negative potentials above, oxygen is discharged. When the current is interrupted the potential of the pole rises very *slowly*. At the end of the above determination the pole was boiled and cooled and the series of values then obtained showed that the pole had not regained its original condition.

Electrolyses with N/10 Potassium Hydroxide.—Curve XI.

Current density.	Potential.	Current density.	Potential.
0	0.639	11.1	—0.270†
0.74	0.590	14.8	—0.319†
1.85	0.543	18.5	—0.344†
2.6	0.528	26.0	—0.369†
3.7	0.467	37.0	—0.381†
7.4	0.405		
11.1*			

The passivizing drop is very slow. The return from the lower potentials also is extremely slow.

The following general conclusions can be drawn from a comparison of the results obtained with the different electrolytes:

(1) The extent of the "impairing effect" wrought by larger current densities upon the anode surface is roughly proportional to the concentration of hydroxyl ions in the electrolyte.

(2) The impairing of the surface in neutral and alkaline solutions may be effected as gradually as may be wished, and this process, as well as the change in potential, is perfectly *continuous* up to the potential with which oxygen is evolved.

(3) The return to high potentials takes place at a rate roughly proportional to the concentration of hydrogen ions in the electrolyte.

I wish to add here that these electrolytic actions produced no noticeable oxide film on the anode.

From (2) above it may be seen that by electrolysis at potentials *above* the discharge potential of oxygen the anode surface may be gradually *saturated* with oxygen—hence the

"impairing effect" is due to discharged oxygen. Evidently this discharge of oxygen begins as soon as the current densities exceed a *very* small limit.

(1) and (2) indicate that the proportional discharge of oxygen with any one current density is greater with alkaline than with neutral solutions, and less with acidified solutions.

I shall now proceed to a general discussion of the facts before us with a view to pointing out their theoretical relations.

As the behavior of the nickel anode in both sulphate and chloride solution with very small current densities is markedly different from the behavior with large current densities, it is likely that the changes which take place under these conditions are different. There is no reason why the change with small current densities should be any other than the ionization of the metal (with solution). The readiness with which the equilibrium potential is attained when the current is interrupted, and other similar indications, support this view. However, this conclusion is inseparably connected with the conclusion that the velocity of ionic solution of nickel at ordinary temperatures must be very small. The idea that metals may differ extensively in their velocity of ionization and that a very small velocity will produce *abnormal* anodic behavior was first advanced by Le Blanc (13). Many indications support the view that nickel has a small ionization velocity. Thus I found that the most concentrated nickel amalgam, when stirred vigorously so as to expose a great deal of new surface which cannot possibly be covered by a protecting film, does not show in N/1 nickel sulphate solution a potential above 0.1 volt, and if more current than that necessary for the electrometer is passed[1] the potential drops lower. It is readily seen that amalgamation may reduce the ionization velocity of a metal, and that with a metal which has, in the solid state, a very small ionization velocity, the reduction may produce a specially marked effect, such as that shown by nickel. However, the low potential may be due to a *specific* property of the amalgam. In this connection, the behavior of iron—the element most

[1] In these trials, air was not excluded. However, it is not likely that the presence of air affected the result, because not the least rise of potential was observed on stirring the amalgam.

closely related to nickel—may be profitably considered. I found that iron amalgam in N/1 ferrous sulphate solution[1] shows a potential of 0.71 volt, which is identical with the potential of solid iron as determined by T. W. Richards and Behr (9). This renders it unlikely that amalgam formation should exert such an enormous specific influence as would be the case with nickel. On searching further in this connection we observe that iron appears to have a greater ionization velocity than nickel. Thus, from the work of Hittorf (4) and of Byers (10) it is seen that to passivize iron in sodium sulphate solution requires somewhat greater current densities than is necessary for nickel. It is also well known that dilute sulphuric acid dissolves iron more rapidly than nickel. Hence it is likely that the ionization velocity of iron is great enough so that even after amalgamation it ionizes rapidly enough to maintain its proper potential; and we may conclude that the inability of nickle amalgam to do so shows that nickel possesses a very small ionization velocity.

The following experiment also furnishes evidence on this point: A nickel anode and the liquid surrounding it (neutral N/1 nickel sulphate solution) were saturated with hydrogen gas and the current of hydrogen was continued during electrolysis. The anode loss that took place under these conditions was determined. The apparatus employed was that described on page 235 with the modification that to the lower end of the test tube was joined a narrow tube through which the hydrogen was introduced. The current density varied from 22 to 26 milliamperes, and the potential from 0.37 to 0.42 volt. The anode lost 0.0430 gram of nickel, while the cathode in the copper voltameter gained 0.4090 gram of copper; thus the loss of the anode is 11 per cent of the current. Hence the nickel ionized corresponding to a current density = 2.4, and in Table I., page 236, we find that nickel alone at the same potential (0.39 volt) supports about the same current density. Since the hydrogen had been passed through the apparatus prior to and during the time that the solution in

[1] Air was carefully excluded in this determination, since it is essential that no ferric ions be present.

it was boiled it is unlikely that any (imperceptibly thin) film of oxide or a layer of oxygen could still be present on the nickel, and since, under these conditions, the nickel does not exhibit a greater ionization velocity than before, this small ionization velocity must be considered to be a specific property of the metal.

This idea is supported further by the influence of temperature. At 95° C., the nickel anode shows a "normal" behavior, which is evidently due to a greater ionization velocity. This is in accordance with our general experience, namely, that increase of temperature accelerates velocities of change.

If it is admitted that the action of the nickel anode at ordinary temperatures with small current densities consists of the direct ionization of the metal, then the different behavior with larger current densities is due to the complication produced by the simultaneous discharge of oxygen —because, as has been pointed out before, the discharge of oxygen also takes place at these high potentials, and there is no reason why the ionization of the metal should cease.

But what effect has the discharged oxygen? This question has been studied in connection with the general problem of passivity, and a review of the results obtained will help to answer the question here. Passivity is exhibited by many metals besides nickel, and has been the subject of many investigations. The recent extensive reviews of the literature of passivity by Fredenhagen (6) and Byers (10) render it unnecessary to make any comprehensive survey at this time. However, it appears to me that there are some facts which have been ommitted, or which have not been properly emphasized, and which may be profitably introduced here.

With the exception of Finkelstein (12) and W. J. Mueller (11)—whose views have apparently not been supported by other workers—and Le Blanc (13)—who suggested that passivity is a phenomenon of ionization velocity—all other investigators have considered that passivity is due to some effect wrought upon the surface of the anode by the discharged oxygen. Some think that the discharged oxygen remains essentially uncombined (Fredenhagen, Muthmann and Fraun-

berger), while many others believe that it forms an oxide film. The protective action of an oxide film is almost "self-evident"; however, to explain all the phenomena of passivity, detailed formulations have had to be elaborated. The two most extensive recently made are by Haber and Goldschmidt (15) and by Erich Mueller (16). They are entirely distinct in most of their essentials. In Haber's theory of "mobile pores" it is assumed that the oxide layer has holes in it which allow the metal to come into direct contact with the electrolyte and to dissolve (ionize!). With very thin (invisible) films—for which the theory is specially formulated—a constant destroying and reforming of the layer is assumed to take place. This results in a constant moving of the pores which expose the metal. Naturally, the relative extent of the areas of the pores and of the oxide cover may vary with the conditions. Erich Mueller's formulation was made in connection with his observation that a copper anode in sodium hydroxide solution exhibits all the characteristic signs of passivity. He observed that the anode is covered with a film, and obtained indications that the evolution of oxygen is due to the decomposition of copper peroxide.

Though all formulations of the oxide theory require that the oxide should have special properties—*e. g.*, it must conduct like a metal—yet the theory has gained much ground because special search has revealed the existence of many such oxides—*e. g.*, copper peroxide, by E. Mueller; platinum oxide, by Ruer (17); iron oxide, by Haber and Kaufmann (18)—and it cannot be denied that such oxides produce all the phenomena connected with passivity.

However, in many cases an oxide film is not apparent, and it has been impossible to detect it by the most refined methods. In such cases the oxide theory requires the assumption that only an imperceptibly thin film is formed. This film, to remain imperceptible, must either give complete protection, so that no more of the metal will be attacked, or it must be dissolved at the same rate at which it is formed. When we consider that many oxides—lead peroxide, iron oxide, aluminium oxide, etc.—do not

protect the metal under them against attack, and when we note the great differences that exist, not only in the solubilities of different oxides, but also of any one oxide, with slight variations in the electrolyte, we realize that this requirement should make the phenomenon much less frequent and less permanent than it is. To emphasize this, we need but point to the fact that a *thick* film of aluminium oxide is formed even in acid electrolytes; that Ruer (17) obtained in 6 per cent sulphuric acid a deposit of platinum oxide which dissolves readily in 50 per cent sulphuric acid, and yet the "passivity" phenomena exhibited by the platinum remain the same as in 6 per cent acid; that Thiel and Windelschmidt (3) found that visible films of nickel oxide might form on the anode at one moment and disappear entirely at the next; and that Foerster and Piguet (1) electrolyzed 2 N potassium hydroxide solution with a nickel anode for 48 hours, and at the end of that time the nickel was as bright as at the beginning.[1]

Altogether there are many special conditions which must be fulfilled before we can have an oxide film that will serve to protect the metal adequately; and it is difficult to believe that these special conditions always obtain. On this account Fredenhagen (14) has proposed his "free oxygen" or "oxygen alloy" theory. He assumes that the lesser solubility and lesser potentials of the anode are due to the fact that the metal is alloyed, or covered, with oxygen, and that the two react very slowly upon each other. He considers this "slow" reaction to be the primary cause of passivity—of the slight solution of the metal while in the passive state, and of the spontaneous return to the active state. Fredenhagen has answered successfully many objections that have been raised against his view.

For the present we are concerned with Fredenhagen's fundamental idea only—that a layer of oxygen gas may protect or

[1] The optical proof of the absence of an oxide film is still a matter of dispute. Mueller and Koenigsberger (19) showed that the least amount of a film of lead peroxide formed could be readily perceived. The observations of Thiel and Windelschmidt (3) on nickel peroxide appear to confirm the result. However, Ruer (22) calculated that he had a layer of platinum oxide *much thinner* than that perceptible by optical methods. There are many other contradictions on this point in the literature, which will be found in the reviews mentioned.

separate a metal surface from the electrolyte, and react very slowly with the metal, although the latter is, in a sense, readily oxidizable. Without any reference to his theory as a whole, I wish to point out that this fundamental idea is well supported by what he has shown, and still more by the following facts.

(1) Sackur's (21) experiments show that a platinum anode polarized with oxygen is practically completely enveloped by it and isolated from the solution. He found that hydrogen which passed by such an anode was practically not oxidized, and since the oxidation of the hydrogen depends upon its being absorbed by the metal, the result indicates that the surface of the platinum is not in direct contact with the solution.

(2) The idea that the oxidation may take place slowly is strange at first sight because we unconsciously attribute the rapid and extensive formation of oxides occasionally observed to this effect. However, many such actions are precipitation actions and not direct oxidations.[1] Erich Mueller and Spitzer (2) have recently set forth the conditions and theoretical relations for such oxide formation. Oxides are readily formed on anodes in alkaline solutions, but they are usually formed when the conditions for their precipitation are fulfilled—*i. e.*, when the solubility product of the metal and hydroxyl ions is reached.[2] But when this is not the case—as in the absence of metal ions in solution, or when the anode does not dissolve—then an oxide is usually not formed. Thus I found that when a nickel anode is introduced into dilute sodium hydroxide while connected in such a way that it closes the current as it enters the electrolyte, no amount of electrolysis will produce any oxide (see also Foerster and Piguet's result quoted above); but if the nickel is allowed to lie in the liquid for 10–15 minutes without being connected *in* the circuit, and then the current is turned on, a heavy coat of black oxide will form on the metal immediately. I have ascertained by trial that no such coat of oxide appears unless the nickel has remained in the liquid

[1] Even in the lead accumulator the transformations take place only through the liquid phase—at least, that is the most logical consideration. See Dolezalek: "Theory of Lead Accumulator."

[2] Naturally this will occur first in the liquid layer next to the anode.

for sometime *without* being anodically polarized, as a result of which it has regained its normal condition (shown by the potential), and hence when the circuit is closed some of the nickel is dissolved before the surface is "impaired" again. In accordance with this is the additional observation that a considerable quantity of oxide is readily formed when the current density is small, whereas no noticeable amount is formed if the current density is very large from the first. The direct oxidation of nickel is not noticeable in this connection.

Striking examples of *slow* oxidation at ordinary temperatures are at hand. Sproesser (20) found that carbon anodes, in the electrolysis of alkali chloride solutions, are oxidized very slightly although the oxygen discharged amounted to 30 per cent of the current used. Sackur (21) has shown that even hydrogen dissolved in and diffusing through dilute sulphuric acid to the anode is oxidized there very slowly. It appears that this state of affairs is rather general.

These experiments indicate that free oxygen may exist on a metal, and protect it in the same manner in which an oxide film would. An oxide may be formed, but its formation is incidental and of no consequence—unless a nonconducting oxide is formed extensively.[1]

If the conditions are such that an oxide with the requisite properties for passivity may be formed, it will appear without disturbing or changing the effect.

[1] It is a particular advantage of the view set forth above that it permits of a simple correlation of anode affects, including "valve action." Such correlation has become possible through two conclusions which can be drawn from the results obtained: (1) That "valve action" of anodes is due primarily to a layer of oxygen gas whose thickness depends upon the thickness of the "oxide skeleton" in which it is embedded (23). (2) That the same metal—*e. g.*, copper (16) and (24), zinc (11) and (23), magnesium (25) and (23)—when acting as an anode, under conditions that remain the same except as regards (*a*) solubility product of oxide and (*b*) anodic potential, may show either normal behavior, passivity, or valve action. As long as the ratio of current density to ionization velocity is not excessive, normal action will be shown. If this ratio is exceeded—either by increasing the current density or decreasing the active surface by precipitation of an oxide, then oxygen will also be discharged, giving rise to passivity phenomena. If an oxide is formed (usually by precipitation) and it is a "conducting" oxide, the anodic polarization remains low, as it is in passivity phenomena and in ordinary polarization on platinum. If the oxide is nonconducting the polarization rises very high—valve effect. Thus, with large current densities a copper anode in copper sulphate solution gives valve action; with moderate current densities, normal anodic behavior; also, in a slightly alkaline solution, with moderate current densities, it gives normal behavior; while with greater current densities or greater concentration of alkali, it gives the passivity effects observed by Erich Mueller.

It is evident that the idea of a "free oxygen cover"[1] has a decided advantage over the "special oxide cover," inasmuch as the conditions for its existence are not as limited as they are for the *special* oxide. But there is no fact which establishes one theory over the other.

This survey of the results obtained in the study of passivity shows us that the effect of the discharged oxygen will be to form an oxide or oxygen gas film which will protect or separate the anode area thus covered from the electrolyte. These areas will be referred to as *oxygen* or oxide spots without any intention of discriminating, because there are no indications in my results incompatible with either idea.

In the behavior of the nickel anode with larger current densities—with which both direct ionization of the metal and discharge of oxygen occur—the following facts require consideration:

(*a*) The lessening of the "active" surface with continued electrolysis.

(*b*) The "quasi" equilibrium conditions with the same current density at different potentials.

(*c*) The lower potentials shown after the current is interrupted—particularly the "air potential."

(*d*) The relation between the rate at which the surface is impaired and the concentration of hydroxyl ions.

(*e*) The relation between the rate of return to higher potentials and the concentration of hydrogen ions.

With the application of larger current densities than those already considered, the discharge of oxygen upon the electrode sets in because the discharge upon an electrode free from oxygen or oxide takes place very easily, and the electrostatic attraction between the pole and the liquid will be great enough. The lessening of the active surface with electrolysis indicates that the discharge of oxygen takes place upon separate spots, rather than uniformly all over the surface. This oxygen may remain as such or it may form an oxide—this is immaterial for the present. The uncovered "active" surface continues

[1] This is only a part of Fredenhagen's theory, and should not be mistaken for the whole.

its activity in sending out ions, and this activity becomes greater as the pole is farther from the point of equilibrium. The *oxygen* or *oxide* spots also exert their tendency to reionize: thus they may prevent partly or wholly the discharge of more oxygen. Two different areas of active surface occurring at different times on the same anode may be so related in distance from the equilibrium potential that they ionize at the same rate and thus support the same current density: this, together with no action on the oxygen spots—as just stated—may be the "quasi" equilibrium conditions. As the current densities are increased the active spots will become smaller and smaller in area. The oxygen may experience something similar to supersaturation, and when such a system "breaks" up, the oxygen spots may encroach *suddenly* upon the active area. This would be the case particularly when large current densities are required, and thus may come about the *sudden* "passivizing" drop often observed. When the current is interrupted, the active spots would not in general show the maximum potential immediately—as would be the case with an anode made up of different metals—instead, the oxygen spots also would begin to ionize, and the two kinds of area would act as a short-circuited cell—the active spots would show a potential depending upon the relative extent of the areas and the concentration in the oxygen spots. This latter will decrease rapidly until its own concentration is in equilibrium with the concentration of the oxygen dissolved in the electrolyte, when it will be "fed" by this, and the potential will remain at this point until the oxygen in the adjacent portions of the liquid is used up.

The observed effect due to a change of acidity or alkalinity in the electrolyte needs very little explanation, because it is plain that the discharge of oxygen out of an alkaline solution will take place more readily—and until the discharged oxygen has attained a greater concentration—than with a neutral solution, and the return to higher potentials will be slower with alkaline than with a neutral solution because the potential of the discharged oxygen in contact with an alkaline solution is less than when in contact with a neutral solution. Thus

the electromotive force of the cell (oxygen spot-electrolyte-active spot) will be less and hence the rate of change will be slower.

This explanation implies that a variation in the concentration of hydrogen ions does not affect the ionization velocity of the metal. That the latter is probably true is indicated by the following results: The polarization curve for N/1 nickel chloride solution (see Curve II.) is not particularly affected when the solution is acidified (see Curve VII.), whereas the polarization curve for N/1 nickel sulphate solution acidified to a corresponding degree is shifted until it falls even beyond Curve VII. (see Curve VI.). Had the variation of the concentration of hydrogen ions affected the ionization velocity of the nickel, then the curve for N/1 nickel chloride solution should have shifted to the right when the solution was acidified.

Finally it may be mentioned that the effect obtained with chloride solutions is considered to be due to the fact that a layer of oxygen is readily attacked by discharged chlorine, and converted to hypochlorite, etc. Thus the impairing of the surface by discharged oxygen is prevented and the current density that the surface can bear is greater. It is also considered that any discharged chlorine reacts quickly upon the metal, in contradistinction to oxygen.

Summary.

1. Nickel has a very small ionization velocity.

2. Most anodic current densities are in excess of the ionization velocity and hence result in the deposition of oxygen. A nickel anode covered with oxygen shows lower potentials than 0.48 volt.

3. The phenomena exhibited by *passive* nickel were studied and the theoretical relation of the ionization velocity and of the deposition of oxygen in these phenomena was pointed out.

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